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MODEL COMPOUND INTERACTIONS
CHARACTERIZING AQUATIC HUMIC SUBSTANCES

by

Joseph Emmanuel Castro

A Thesis Submitted to the Faculty of the

DEPARTMENT OF CIVIL ENGINEERING AND ENGINEERING MECHANICS

In Partial Fulfillment of the Requirements
For the Degree of

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WITH A MAJOR IN CIVIL ENGINEERING

In the Graduate College

THE UNIVERSITY OF ARIZONA

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STATEMENT BY AUTHOR

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Date

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I thank my family who has always been there for encouragement and support, and Kimberley who helped me get through this long task.

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ABSTRACT

An attempt was made to simulate XAD-8 isolates of Orange County groundwater and Biscayne Aquifer groundwater using mixtures of single ligands. Mixtures of catechol, glycine, phthalic acid and salicylic acid were used to simulate potentiometric and complexometric titrations. Concentrations used for the mixtures were based on carboxylic acidity, dissolved organic carbon, and assumed values for phenolic acidity and nitrogen content. Potentiometric titrations were reproduced with mixtures of the ligands; however, complexometric titrations at pH 6.2 and pH 7.5 could not be duplicated. A stronger ligand was required to fit the pH 6.2 titrations, and higher carboxylic contents were needed for pH 7.5. At pH 6.2, 70 percent of the binding sites were attributed to phthalic acid-type groups and 20 percent to catechol-type groups. At pH 7.5 greater than 98 percent was attributed to phthalic acid-type groups.

CHAPTER 1

INTRODUCTION

Organic matter leaches from plants and soil matter enters natural systems and becomes dissolved organic carbon (DOC) or particulate organic carbon (POC). DOC is operationally defined as the fraction of organic carbon that passes through a 0.45-micron filter. Of the DOC, approximately 50 percent or more is typically present as humic substances. These humic substances are a concern in drinking water supplies and in the transport of trace metals in the environment.

The modeling of humic substances can only achieve limited success with fitting experimental data with model parameters. The advance in computer technology has allowed even more sophisticated statistical packages that can readily analyze a set of data.

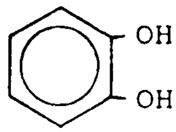
1.1 Objectives

Humic substances are known to complex trace metals in the environment and increase the solubility and movement of these metals. A clear and complete structure of a humic substance is not available although representative structures have been postulated (Schnitzer and Khan, 1972;

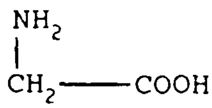
Olofsson and Allard, 1983; Steelink, 1985). Understanding the complex nature of humic substances may help predict the role they have in the fate of metals. Attempts to model metal binding by humic substances have not been successful due to unambiguous determinations of the functional groups concentrations responsible for binding. Along with that has been the overlooking of the mathematical properties of complex multi-ligand mixtures (Perdue, et al., 1984). This author attempted to develop a simple model of a humic substance by approximating the actual distribution of functional groups and the complexation behavior using model ligands. Verifying probable chemical structures of two sources of humic substances was performed by reproducing actual titration curves.

From the postulated structures of a fulvic and humic acid, carboxylic, phenolic, and amino groups were reproduced. Catechol, phthalic acid and salicylic acid represented the carboxylic and phenolic content (see Figure 1.1). Glycine was used as the amino acid due to the high binding constant for Cu(II)-glycine complexes and the high content of glycine (Thurman, 1985).

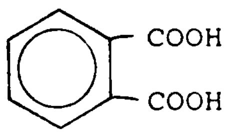
The dissolved organic matter for this research came from two groundwater sources: Orange County, California, and the Biscayne Aquifer, Florida. Orange County groundwater (OCGW) has approximately 80 percent of its DOC as humic matter and the Biscayne Aquifer (BA) has approximately 50



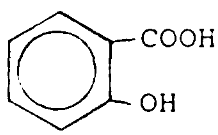
catechol



glycine



phthalic acid



salicylic acid

Figure 1.1 Model compound structures

percent (Amy, et al., 1989). The use of these groundwaters was advantageous due to the following reasons:

i) Accessibility of both waters to the University of Arizona Environmental Engineering Department,

ii) OCGW has been previously investigated (Waterbury, 1990),

iii) BA has been previously investigated (Thurman and Malcolm, 1981),

iv) the use of two different sources may further validate the modeling effort, and

v) the current need for the direct study of groundwater chemistry (Holm and Curtiss, 1990).

Copper was used as the trace metal of interest due to its high affinity towards ligands, its ubiquity in the environment, the numerous studies already conducted on Cu(II) speciation, and the availability of ion-selective electrodes to measure free copper(II) during titrations.

Complexometric titrations were conducted at pH 6.2 and pH 7.5 to study the effects of increasing pH while still maintaining the natural state of groundwaters, pH 6 to 8.

1.2 Experimental Plan

Potentiometric and complexometric titrations were first conducted on the model compounds to validate published values and experimentally-determined values under controlled pH and ionic strength. Validation of dissociation and binding constants of the model compounds was conducted by comparing experimental curves with theoretical curves. Titrations of the natural sources were then performed and

modeled with representative concentrations of the model compounds from measured carboxylic contents and assumed phenolic and nitrogen contents. Model mixtures were then titrated both potentiometrically and complexometrically to validate the proposed model humic substance.

CHAPTER 2

BACKGROUND

The portion of organic matter known as humic substances has been described by Schnitzer and Khan (1972) as follows:

> "amorphous, brown or black, hydrophilic, acidic polydisperse substances of molecular weights ranging from several hundreds to tens of thousands."

They further subdivided humic substances into three main fractions based on solubility and acidity:

i) humic acid (HA), which is soluble in dilute alkaline solutions but is precipitated by acidification of the alkaline extract;

ii) fulvic acid (FA), which is that humic fraction which remains in the aqueous acidified solution; and

iii) humin, that fraction which cannot be extracted by dilute base and acid.

2.1 **Elemental Composition**

A description of a humic substance will depend on the source and type. Groundwater sources tend to have humic substances that are aliphatic in nature, less aromatic, less humified, and of lower molecular weight than those in soils and surface waters (Boggs, et al.,1985). They are also richer in carbon but lower in oxygen and nitrogen than soil humics. As far as the type of humic substance, humic acids contain more carbon and nitrogen and less oxygen than fulvic

acids (Schnitzer and Khan, 1972). HA also have larger molecular weights than FA and are thought to be degraded to fulvic acids.

Several elemental distributions and ratios for groundwater humic substances are shown in Table 2.1. Some of the trends discussed above can be seen in the examples shown on the table. Amino acids account for 15 percent of the nitrogen in aquatic fulvic acid and 20 percent of the nitrogen in aquatic humic acid (Thurman, 1985). Tables 2.2 and 2.3 show concentrations of amino acids from different sources and the types present.

Table 2.1 Elemental composition and ratios of groundwater humic acids (HA) and fulvic acids (FA)

Percentages							
Source:	C	H	N	S	O	P	Ref.
FA Avg.	40-50		<1-3	0-2	44-50		Schnitzer and Khan (1972)
Biscayne FA	55.44	4.17	1.77	1.06	35.39	0.2	Thurman and Malcolm (1981)
Suwannee FA	54.65	3.71	0.47	0.5	39.28	0.2	"
Model FA	45.7	5.4	2.1	1.9	44.8		Schnitzer and Khan (1978)
HA Avg.	40-60	4-6	1-6	0-2	30-50		Lamy, et al., (1987)
Biscayne HA	58.28	3.39	5.84	1.43	30.14	0.22	Thurman (1981)
Suwannee HA	57.24	3.94	1.08	0.63	39.13	0.2	"
Model HA	56.2	4.7	3.2	0.8	35.5		Schnitzer (1978)

Ratios			
	H/C	O/C	N/C
Biscayne FA	0.69	0.39	0.09
Suwannee FA	0.82	0.51	0.06
Biscayne HA	0.90	0.47	0.03
Suwannee HA	0.81	0.54	0.01

Table 2.2 Concentration of amino acids in soil and aquatic humic substances (Thurman, 1985)

Sample	Amino Acids (nM/mg)
Groundwater	
Fulvic	29 - 44
Humic	121
Streams and Rivers	
Fulvic	14 - 127
Wetlands	
Fulvic	36 - 79
Humic	112
Soils	
Fulvic	145 - 170
Humic	478 - 707

Table 2.3 Average concentration of amino acids present in humic and fulvic acids from water (Thurman, 1985)

Amino acid	Concentration (nM/mg) FA	HA
Acidic		
Aspartic acid	5.7	12
Glutamic acid	3.0	9
Adipic acid	0.5	0.7
Neutral		
Glycine	11	22
Alanine	3	10
Leucine	1	4
Isoleucine	1	3
Valine	1	5
Serine	2	5
Threonine	2	6
Secondary		
Proline	2	8
Hydroxyproline	1	17
Aromatic		
Phenylalanine	0.5	2
Tyrosine	0.5	1
Basic		
Arginine	1	1.4
Lysine	0.5	2.5
Histidine	0.2	1.3
Sulfur		
Cystine	0.2	0.7
Methionine	0.2	0.7
Total	36	110

2.2 Functional Groups

Although the actual structure of both the HA and FA fraction are unknown, it is composed of a series of functional groups; the major functional groups are shown in Figure 2.1. Functional groups of a model HA and FA determined by Schnitzer and Khan (1978) are shown in Table 2.4. Liao, et al. (1982), using gas chromatography/mass spectrometry on surface water from lakes, found that the general molecular structure of aquatic humics consisted of (a) single-ring aromatics with mainly three to six substituents as alkyl side chains, carboxylic acids, ketones, or hydroxyl groups; (b) short aliphatic carbon chains; and (c) polycyclic ring structures including polynuclear aromatics, polycyclic aromatic-aliphatics, and fused rings. In river waters and lakes, Plechanov, et al. (1983), used H-NMR (nuclear magnetic resonance) and found compounds present to be lignin-derived and of alkyl groups. Steelink (1985) has proposed basic units that are composed of postulated functional groups (see Figure 2.2). Others have postulated a representative structure for a FA and HA as shown on Figure 2.3. What is not shown in these structures are the small percentages (< 2 percent) of both nitrogen and sulfur (Perdue, 1985).

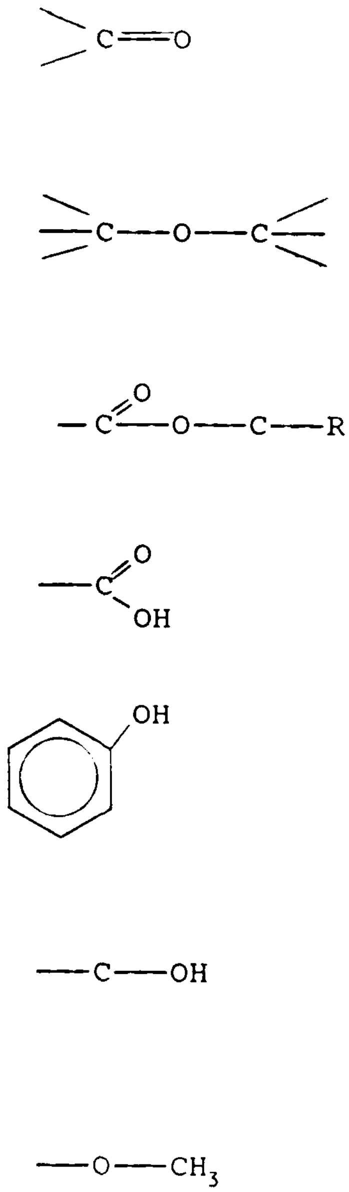


Figure 2.1 Major functional groups in humic substances (after Snoeyink and Jenkins, 1980)

Table 2.4 Functional group composition (Schnitzer and Khan, 1978)

Functional Groups	Model HA (meq/g)	Model FA (meq/g)
Total Acidity	6.7	10.3
COOH	3.6	8.2
Phenolic -OH	3.9	3.0
Alcoholic -OH	2.6	6.1
Quinonoid C=O Ketonic C=O	2.9	2.7
OCH_3	0.6	0.8
E_4/E_6 *	4.8	9.6

$$* \ \frac{\text{absorbance at 465 nm}}{\text{absorbance at 665 nm}}$$

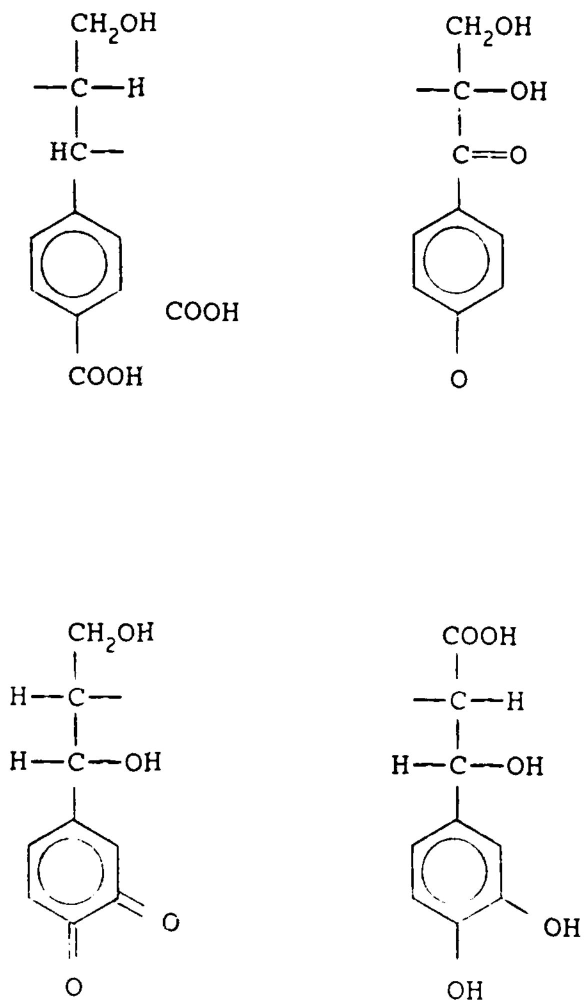


Figure 2.2 Proposed basic units in humic acids (after Steelink, 1985)

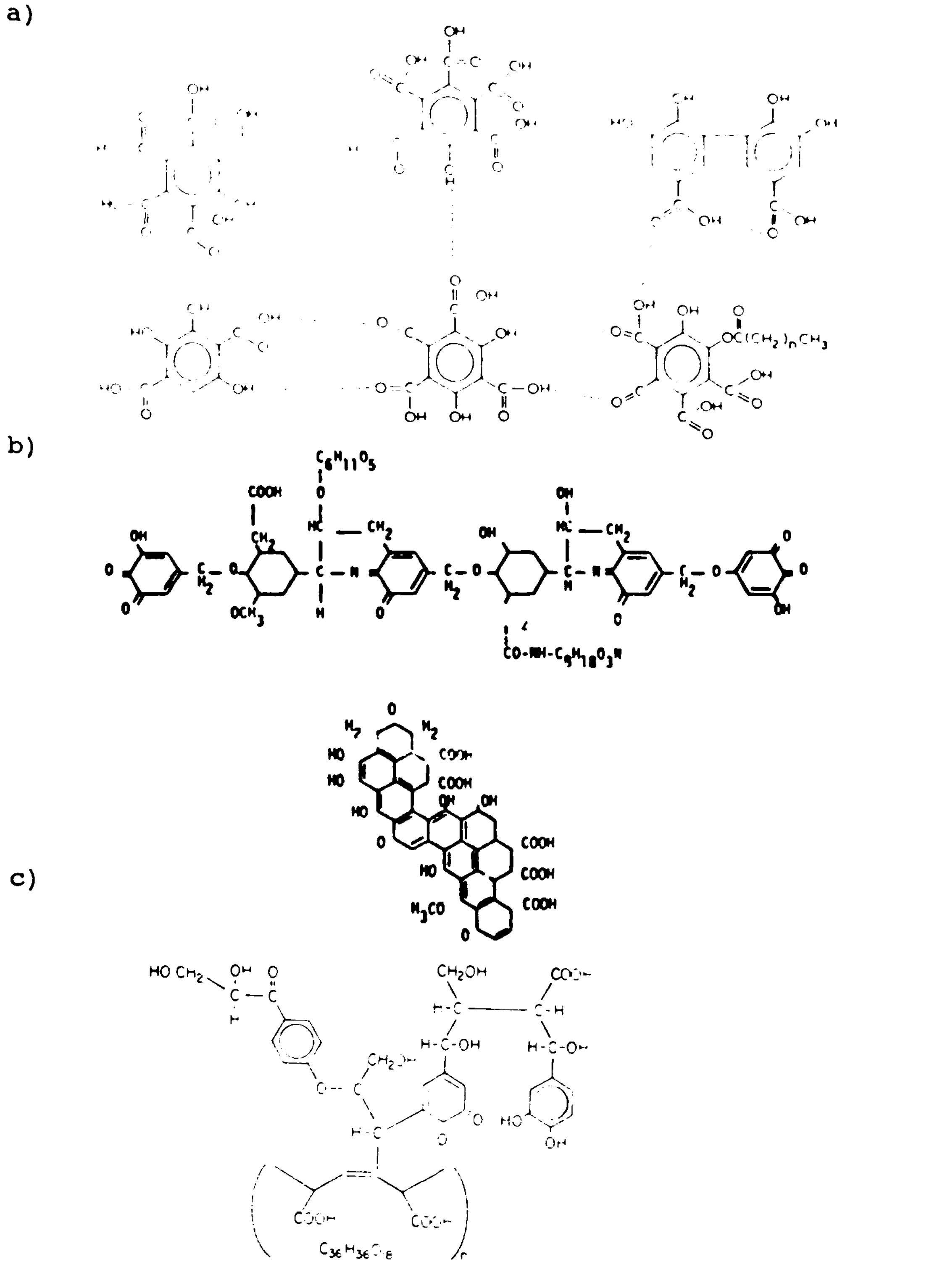


Figure 2.3 Postulated structure of a) fulvic acid (Schnitzer and Khan,1972), b) humic acid (Oloffson and Allard, 1983) and c) humic acid (Steelink, 1985)

Several researchers have postulated on which types of functional groups in humic substances are important in the complexation of metals. Gamble (1970) has postulated that salicylic-type groups are involved in metal complexation while Manning and Ramanoorthy (1973) have suggested that the phthalic-type groups were responsible. Schnitzer (1972) suggested that both types of groups were important with the addition of C=O type groups and amines. Buffle, et al. (1980) refuted the idea that salicylic- and phthalic-type groups were solely responsible. By comparing the complex-formation properties of different natural water samples with the binding capacities of salicylic and phthalic acids, they showed that the binding was not high enough to satisfactorily explain the complexing properties of a fulvic acid by copper. McKnight, et al. (1983), modeled the complexation of aquatic fulvic acids by copper using two concentrations and binding constants. The most abundant ligand site (L_1) represented both salicylic- and phthalic-type acids but only 16 percent of the total functional groups. The second most abundant ligand (L_2) only represented 5 percent of the carboxylic and phenolic functional groups. There was also a high variability of L_2 concentrations among the samples. They attributed the variable concentrations of functional groups to trace concentrations of possibly nitrogen and/or sulfur. More recently, Ephraim, et al. (1989), identified 30 - 45 percent

of the acidic sites responsible for copper binding as a salicylic acid-like moiety and 25 - 30 percent as a catechol-like moiety for an aquatic fulvic acid. Shown in Table 2.5 are dissociation and binding constants of some of the proposed types responsible for metal binding.

Table 2.5 Dissociation and binding constants of possible binding groups

Published Values	Catechol (H_2L)	Glycine (HL)	Phthalic (H_2L)	Salicylic (H_2L)
	Model Compounds			
Potentiometric				
pK_{a1} ($HL/H \cdot L$)	13.0	9.57	4.93	13.6
pK_{a2} ($H_2L/HL \cdot H$)	9.23[1]	2.36[1]	2.75[1]	2.80[2]
Complexometric				
B_1 ($ML/M \cdot L$)	13.58[3]	8.27[4]	4.00[1]	10.80[2]
B_2 ($ML_2/M \cdot L^2$)		15.19[4]	5.31[5]	18.45[6]
($MHL/M \cdot HL$)			1.20[1]	
($ML \cdot H/M \cdot HL$)	0.85[7]			
($ML \cdot H^2/M \cdot H_2L$)	-8.345[7]			

[1] Smith and Martell, 1975
[2] Condike and Martell, 1969
[3] Athavale, 1966
[4] Greiser and Sigel, 1971
[5] Lumme and Kari, 1975
[6] Neshkova and Sheytanov, 1985
[7] Jameson and Wilson, 1972

2.3 Metal Complexation

Humic substances are ubiquitous in the natural environment and are good ligands for metal binding. Humics can be important in the solubility of toxic metals in water sources and in the kinetics of transporting these metals (Clark and Choppin, 1990). Mantoura, et al. (1978), and Perdue (1989) described the main factors that control metal-humic interactions with the following:

i) value of the binding constant; i.e., the nature of the metal and the binding site,

ii) elevated pH that causes increased binding,

iii) humic substance concentration,

iv) elevated ionic strength that causes decreased binding, and

v) major ion concentrations that control the competition for humic acid by magnesium and calcium, and the competition for trace metals by chloro- or sulphato- ligands.

Guy and Chakrabarti (1976) used a commercially-available humic acid (Aldrich) at pH 5 and found the stability constants of metal-organics to decrease as follows:

$$Pb(II) > Cu(II) > Cd(II) > Zn(II) .$$

They also found that humic acids can maintain the binding of metal ions to as low as pH 3. Takamatsu and Yoshida (1978) also found increasing binding constants with pH for several soil humic acids, but unlike the previous authors, they found Cu(II) to have higher binding than Pb(II), and Cd(II) to have significantly lower binding at pH 5. Schnitzer and

Khan (1978), at pH 5.8 with soil-derived fulvic acids, showed the following binding trends:

$$Hg = Fe = Pb = Al = Cr = Cu > Cd > Zn > Ni > Co > Mn \ .$$

Dobbs, et al. (1989), also recently showed the increase in metals bound with an increase in the number of binding sites.

Of the metals available for binding by humic substances, copper (II) is the most studied. Copper is a concern to the environment due to its toxicity to aquatic organisms. Copper toxicity is dependent not on the total copper concentration but on free copper activity (Anderson and Morel, 1978; Sunda and Guillard, 1976). Sunda and Hanson (1979) found through the UV-photooxidation of organic matter in river waters that the copper was bound predominantly to organic ligands. This directly affects the toxicity and bioavailability of copper to organisms as well as copper adsorption onto surfaces, copper precipitation, and solid solubility. It is therefore important that metal-humic interactions be part of any computational scheme in any modeling of natural water systems (Bassett and Melchior, 1990).

2.3.1 Mathematical Models

Some attempts to mathematically model the affinity of metals to humic substances were derived from earlier attempts of modeling proton binding to acidic polymers, ion exchange resins, and so on (Perdue, 1985). Current metal-

humate models are similar in the assumptions that follow:

i) reactions at individual sites (ligands) are governed by mass law equations, and

ii) microscopic mass law constants do not change with increased metal loading, i.e., there are no interactions among sites (Dzombak, et al., 1986).

Discrete and continuous multi-ligand models are currently used to describe metal-humate interactions.

The discrete ligand model uses only a few ligands (< 10) to fit experimental data. Dzombak, et al. (1986), noted that the optimal number of ligands can be estimated as one ligand for each order of magnitude of bound metal concentration observed in the titration data. Perdue (1985) described the discrete ligand model as inappropriate due to the complex mixture of nonidentical ligands that are expected in humic substances. The goal of this model though is not to represent a humic substance but to represent those sites that are important in metal binding and are of the most use (Fish, et al., 1986).

The continuous distribution models include the normal distribution model, the affinity spectrum model and the continuous stability function model. These models are based on the assumptions that the binding constant of a humic substance to a metal varies continuously and that the ligand frequency distributions can be integrated over the varying binding constant. Continuous distribution models offer an integral solution for ligand distributions, but the solution

is complex and numerical attempts to solve the integral equation are plagued by spurious oscillations (Dzombak, et al., 1986). A solution to the problems with the continuous distribution models is to assume a distribution. Such is the case with normal or Gaussian distribution models in which the probability of occurrences for a given ligand is assumed to be described by the symmetrical Gaussian distribution function (Perdue, 1985). Due to the generality of the theoretical normal distribution, the model only becomes useful as a good first approximation of the most probable acidic functional groups responsible for binding metals. The affinity spectrum model attempts to avoid the problems associated with solving an integral equation through the use of an affinity spectra. Peaks in the affinity spectrum reflect the importance of certain ligands and can be used as an aid for selecting discrete ligands from experimental data (Dzombak, et al., 1986). A similar model developed by Gamble, et al. (1972, 1973, 1980, 1983) is called the continuous stability function model. The approach in this model is to chose a dominant binding constant at each titration point and fit a ligand concentration to it. Shortfalls, however, include the characterization of only the weakest and most abundant ligand in a distribution (Dzombak, et al., 1986).

It should be recognized, though, that with metal-binding interaction, as the number of components or ligands

that bind the metal increase so does the number of sites for binding. The result is a smooth curve that can be modeled fairly easily, and if fitted, the output is only curve-fitted values.

2.3.2 Mathematical Applications

Current geochemical models experience difficulty incorporating humic substances into speciation calculations (Bassett and Melchior, 1990). The problem is due to the complex nature of humic substances. Classical attempts such as the Debeye-Huckel equation cannot be applied.

Perdue (1978) described the generalized reaction of a metal (M) and a protonated ligand complex (HL) to a complexed metal (ML) with the following expression:

$$M + HL \; === \; ML + H^{+} \qquad (1)$$

This equation is thermodynamically equivalent to the following:

$$HL \; === \; H^{+} + L \qquad (2)$$

and

$$M + L \; === \; ML \qquad (3)$$

The knowledge of dissociation constants helps to better understand the concentration and chemical characteristics of humic substances.

Direct potentiometric titrations can give operationally-defined estimates of carboxylic groups which relate to dissociation constants for the humic substance(Perdue, 1980; Oliver, et al., 1983). Currently, operationally-defined carboxylic content is that acidity

required to titrate a solution from pH 3 to 8, and phenolic content is estimated at twice the acidity required to titrate from pH 8 to 10 (Thurman, 1985). Phenolic content taken as the difference between total acidity and carboxylic content has, however, not achieved complete certainty (Perdue, et al., 1980).

The binding of copper by DOC can assume the simplest form according to Cabaniss and Shuman (1988a) with a 1:1 complex stoichiometry, no site interactions, and a single binding site of concentration L_T. The binding constant expression (see Table 2.6 for term definitions)

$$K_{Cu} = \frac{[CuL]}{[Cu]\,[L]} \tag{4}$$

rearranges to the form below to give the concentration of bound copper, [CuL],

$$[CuL] = \frac{[L_T]\,[Cu]\,K_{Cu}}{1 + [Cu]\,K_{Cu}} \tag{5}$$

If the simplifying assumptions are dropped, the model gets more complicated.

When the assumption that all the binding sites within the humic acid are identical is dropped, [CuL] is expressed as follows (Cabaniss and Shuman, 1988a):

$$[CuL] = \sum_{i=1}^{N} \frac{[L_T]\,[Cu]\,K_{Cu}}{1 + [Cu]\,K_{Cu}} \tag{6}$$

Models such as the discrete ligand, continuous distribution, and normal distribution model make different assumptions of

Table 2.6 Terms and definitions (after Cabaniss and Shuman, 1988a; Neshkova and Sheytanov, 1985)

$[Cu_T]$	total copper concentration
[Cu]	cupric ion concentration
[CuL]	copper-organic complex concentration
[L]	free ligand concentration
[CuOH]	hydrolyzed copper concentration
[CuOHL]	hydrolyzed copper-ligand complex concentration
N, i	number of binding sites, site being considered
$[L_T]$	total ligand concentration
$[L_i]$	concentration of ligand i
{H}	proton activity
P, j	maximum coordination number, number being considered
B_j	copper binding constant for j ligand molecules
K_{cu}	copper binding constant for 1:1 complex
K_H	proton binding constant
K_a	apparent K_{cu} for given charge on polyelectrolyte
K_{CuH}	copper-proton exchange constant
K_{CuHH}	copper-proton^2 exchange constant
K_{OH}	copper hydrolysis constant
K_{CuOH}	hydrolyzed copper-ligand binding constant
$\alpha_{L(H)}$	side-reaction coefficient for protonation of a ligand (see eqn. 18)
T	temperature (°K)

equation (6) about the number and distribution of sites.

If the assumption that the complex stoichiometry is greater than 1:1 [i.e., 1:2 to a maximum of 1:6 with Cu(II)], then a single binding site can be expressed as

$$[CuL] = \sum_{j=1}^{P} B_j \; [Cu] \; [L_j] \tag{7}$$

Proton dependence must be accounted for in any model. A first-order proton dependence will have the binding as shown below (Gamble, et al., 1980):

$$K_{CuH} = \frac{[CuL]}{[Cu] \; K_H \; [L]} \tag{8}$$

where

$$K_H = \frac{[HL]}{\{H\} \; [L]} \tag{9}$$

or

$$K_{CuH} = \frac{K_{Cu}}{K_H} \quad \text{for} \quad [L] << [HL] \tag{10}$$

The bound copper will be

$$[CuL] = \frac{[L_T] \; [Cu] \; K_{CuH}}{\{H\} + [Cu] \; K_{CuH}} \tag{11}$$

If the dominant species of the ligand is in the form H_2L, then bound copper is expressed as

$$[CuL] = \frac{[C_T] \; [Cu] \; K_{CuH}}{\{H\} + [Cu] \; K_{CuH}} \tag{12}$$

or

$$[CuL] = \frac{[C_T]\ [Cu]\ K_{CuHH}}{\{H\}^2 + [Cu]\ K_{CuHH}} \qquad (13)$$

If the bound copper is being hydrolyzed or a hydrolyzed copper is being bound then the binding of hydrolyzed copper can be expressed as

$$K_{CuOHL} = \frac{[CuOHL]}{[CuOH]\ [L]} = \frac{[CuOHL]\ \{H\}}{[Cu]\ K_{OH}\ [L]} \qquad (14)$$

where

$$K_{OH} = \frac{[CuOH]\ \{H\}}{[Cu]}, \qquad (15)$$

and the hydrolyzed copper is

$$[CuOHL] = \frac{[L_T]\ K_{CuOHL}\ K_{OH}\ [Cu]}{\{H\} + K_{CuOHL}\ K_{OH}\ [Cu]} \qquad (16)$$

The above equations are used for theoretical and modeling calculations, but for more applicable use, the binding constants can be determined from experimental data with the following expressions (Neshkova and Sheytanov, 1985):

$$[Cu] = [Cu_T]/(1 + B_1 \frac{[L_T]}{\alpha_{L(H)}} + B_2 \frac{[L_T]^2}{\alpha^2_{L(H)}} + \ldots B_n \frac{[L_T]^n}{\alpha^n_{L(H)}}) \qquad (17)$$

where

$$\alpha_{L(H)} = 1 + \{H\}\ K_H + \{H\}^2\ K_H\ K_{2H} + \ldots \{H\}^n\ K_H\ K_{2H} \ldots K_{nH} \qquad (18)$$

Temperature effects for titration data can be corrected

by the following equation (Smith and Martell, 1975):

$$\log K_{Cu2} = \log K_{Cu1} + \Delta H(T_2 - T_1)/1701.3654 \text{ KJ } ^{o}\text{K/mole} \quad (19)$$

where ΔH is the enthalpy change.

Ionic strength corrections are tabulated in Smith and Martell (1975). They found that stability constants usually decrease with increasing ionic strength and generally reach a minimum at an ionic strength of about 0.5. Stability constants were also observed to increase through an ionic strength of at least 3.0, and ionic strengths of 0.1 and 1.0 frequently had the same magnitude.

2.3.3 Model Fitting

Copper titration data can be fitted with any of the above modeling methods to obtain parameters. Although these fitting parameters are operational binding constants and are highly dependent on experimental conditions, comparing metal speciation that was computed with model parameters is appropriate (Holm and Curtiss III, 1990). It is, however, inappropriate to compare complexation parameters determined by different methods or for different water samples (Cabaniss and Shuman, 1988c). For this reason, only a few modeling attempts will be discussed. Van Den Berg and Kramer (1979) assumed the simplest binding of 1:1 of copper with no proton dependency, and they obtained binding constants for a fulvic acid and ligands in Lake Ontario of $10^{7.8}$ and $10^{8.8}$, respectively. They calculated these constants with no knowledge of the dissociation constant of

the water sample and at a pH of 7.6.

A discrete ligand model was used by Hering and Morel (1988) for a Suwannee Stream humic acid at pH 8.2 to 8.3. They obtained the best fit with a 3-ligand system at concentrations of 5.0×10^{-5} M, 2.0×10^{-4} M and 1.8×10^{-8} M with binding constants of $> 10^{11}$, $10^{9.2}$ and $10^{6.6}$, respectively. Copper titrations were done at pH 8.2 to 8.3. In comparison, Cabaniss and Shuman (1988b) modeled Suwannee fulvic acid with a 5-ligand system for the pH range of 5 to 8.5.

Groundwater from Orange County, California, was titrated by Waterbury (1990) and the best fit was obtained using a 2-ligand system. He modeled an XAD-8 humic acid fraction with L_1 at $10^{-7.5}$ and L_2 at $10^{-11.2}$ with binding constants of pL_1 at 5.2 and pL_2 at 4.9 for pH 6.2 and an ionic strength of 10 mM.

2.4 Chemical Models

In the attempt to attribute some chemical significance to the structural and modeling work, several researchers have used different chemicals. EDTA (Dursma, 1970), nitrilotriacetic acid (Childs, 1971), salicylic acid (Morel and Morgan, 1972), and citric acid (Stumm and Brauner, 1975) were some of the single compounds tried in the modeling of a humic substance. Bresnahan (1978) attempted a 1:2 and a 1:1 mixture of salicylic and phthalic acid to simulate a soil fulvic acid but also had no success. Lamy, et al. (1987), did not try to simulate a humic substance but went directly to a commercially-available humic-like substance called PCTG (catechol + triglycine polycondensate). PCTG had the following elemental composition in percentages:

C - 45.4, H - 4.0, N - 11, O - 36.9, S - 0.5.

All of the percentages fell within the average composition of a humic acid with the exception of the nitrogen content, which was high.

Strict adherence to elemental compositions will not by itself describe a humic substance. Steelink (1985) showed that chemical formulas of humic substances can also describe the same empirical formula for whole wood. Elemental composition can help one devise hypothetical structures for humates.

CHAPTER 3

MATERIALS AND METHODS

The stages of this research included (1) the selection and verification of model compounds, (2) the titrations of two XAD-8 isolates, and (3) the modeling with experimental verification. The two XAD-8 isolates were groundwaters from Orange County and the Biscayne Aquifer.

3.1 **Materials**

3.1.1 Chemicals

All chemicals used for this research were reagent grade. Adjusting of pH was done with diluted concentrations of HNO_3 (1.0 N, 0.1 N, and 0.01 N) and NaOH (1.0 N, 0.1 N, 0.08 N, and 0.01 N). Distilled water passing through a Millipore cartridge system (referred to as Milli-Q water) was used for dilutions.

pH control was accomplished with the zwitterion buffer MES (4-morpholineethane sulfonic acid, Aldrich) for pH 6.2 and HEPES [1,4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid, Aldrich] for pH 7.5. Ionic strength was adjusted to 10 mM with sodium nitrate (Mallinckrodt). Copper (II) nitrate [$Cu(NO_3)_2 \cdot 3H_2O$, Alfa] was used. Determining the concentration of the stock solution of copper was accomplished with EDTA titrations(Nutritional Biochemicals Corp.).

The model compounds used were catechol (1,2-dihydroxybenzene, Aldrich); glycine (aminoacetic acid, Baker); phthalic acid (benzene-1,2-dicarboxylic acid, Aldrich); and salicylic acid (2-hydroybenzoic, Aldrich).

All of the labware used was acid washed. Washing consisted of rinsing and then soaking in a 3:1 (Milli-Q:HNO_3) nitric acid bath for 8 hours. Rinsing and soaking in Milli-Q followed for at least 3 hours.

3.1.2 Groundwater Samples

The two sources of humic substances were from groundwaters collected in five-gallon polypropylene containers in Orange County Water District, California, and the Biscayne Aquifer in Dade County, Florida. Upon receipt, samples were stored at 4° C as received. Groundwaters were filtered with prewashed 0.45-μm filters to isolate dissolved organic matter (DOM). From analyses provided by Orange County Water District and specific conductance measurements, the ionic strength of OCGW was determined to be 3 mM (Waterbury, 1990). BA groundwater had a similar conductivity measurements and ionic strength as OCGW. Characteristics of the XAD-8 isolates are shown in Table 3.1.

Table 3.1 Characteristics of humic fraction (Odem, 1990)

Source	DOC (mg/L)	Humic %	pH	Avg. MW	Conductivity (uohms/cm)	COOH Acidity (meq/g-C)
OCGW						
XAD-8	5.23	80	7.95	1700	420	19.7
BA						
XAD-8	5.66	50	8.05	1600	480	13.4

3.2 Analytical Methods

3.2.1 Organic Carbon

Concentrations of dissolved organic carbon were measured with a Shimadzu Model TOC-500 carbon analyzer. Standards were at 5.0 and 10.0 ppm DOC. Prior to injection, a 10-ml sample was acidified to pH 2 - 3 and purged for ten minutes with N_2 gas. Injection volume was 50 μl.

3.2.2 pH and Cu^{2+}

pH and free copper was measured with a Fisher Scientific Accumet 950 pH/ion Meter. The pH probe used was a Radiometer America pH electrode, and the copper probe was an Orion cupric electrode in combination with an Orion double junction reference electrode. The pH was calibrated with pH 4.00, 7.00, 8.00, and 10.00 buffers (Metrepak) in combination with a Fisher Scientific automatic temperature probe. Cupric electrodes were calibrated with 10^{-6} M, 10^{-5} M, and 10^{-4} M $Cu(NO_3)_2$ adjusted to an ionic strength of 10 mM and pH 6. Copper standards and titrants were made in polypropylene, 100-ml beakers from a stock concentration of 0.3707 M $Cu(NO_3)_2$. Standard were made weekly and titrants daily. The stock Cu(II) was kept refrigerated at 4° C between uses. Linear regressions from the millivolt responses of the copper standards provided a standard curve for free copper concentrations. A typical copper calibration curve is shown in Figure 3.1. For this standard curve, dilutions of 10^{-7}, 10^{-6}, 10^{-5}, and 10^{-4} M were measured

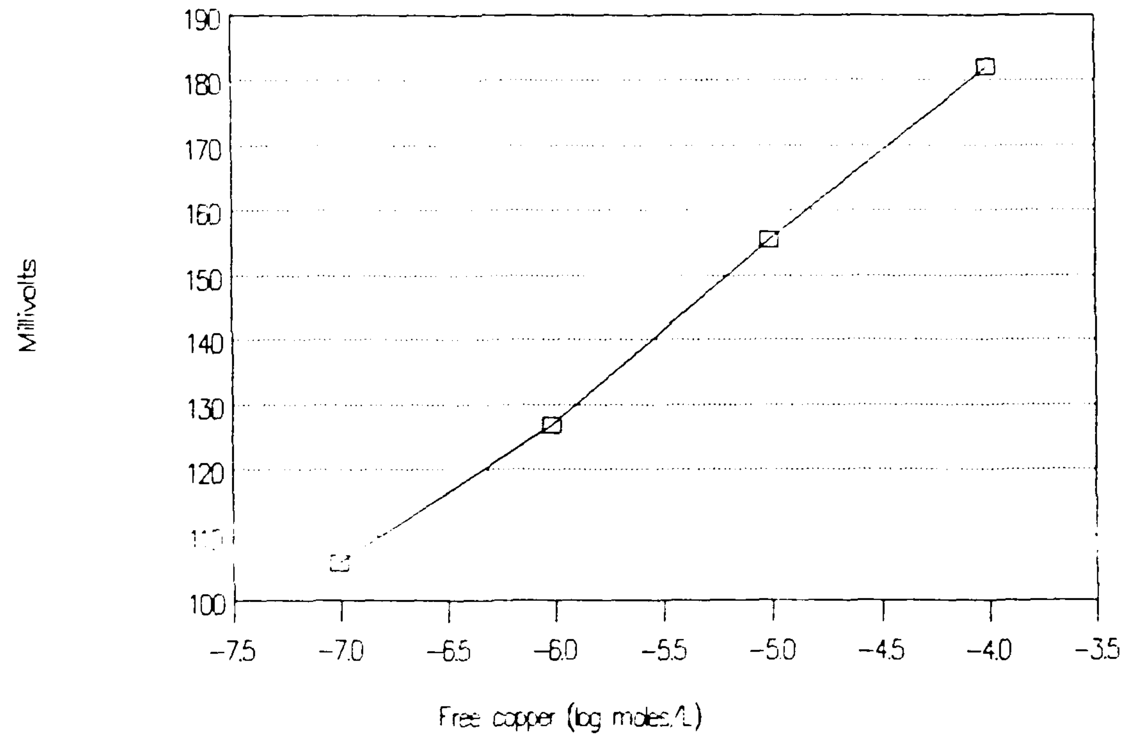


Figure 3.1 Typical copper (II) calibration curve

with the copper probe and plotted. A linear regression done with Quattro spreadsheet software yielded the following expression for 10^{-4} to 10^{-7} M:

$$\log [Cu] = 0.038786 (mV) - 11.0349 . \qquad (20)$$

The r^2 for this range was 0.996. Since the linear response of the copper probe becomes non-linear below approximately $10^{-6.7}$ M (Orion, 1986), a three-point standard curve was used for concentrations of 10^{-6}, 10^{-5}, and 10^{-4} M for the complexometric titrations. For the same standard curve shown in Figure 3.1, the linear expression changed to

$$\log [Cu] = 0.0363 (mV) - 10.6248, \qquad 21)$$

and r^2 was 0.999. Linearity assumed to 10^{-7} M had only slight deviations.

3.2.3 EDTA Titrations

EDTA titrations using the cupric electrode probes were performed on the diluted stock copper (II) solution as described in the cupric electrode instruction manual (Orion, 1986). Figure 3.2 shows two titrations conducted. The inflection point on the curves indicated the concentration for the stock copper (II) solution to be the following:

Titration A: 0.3680 M

Titration B: 0.3730 M

The mean of the two titration curves of 0.3707 M was used for the stock copper (II) solution concentration.

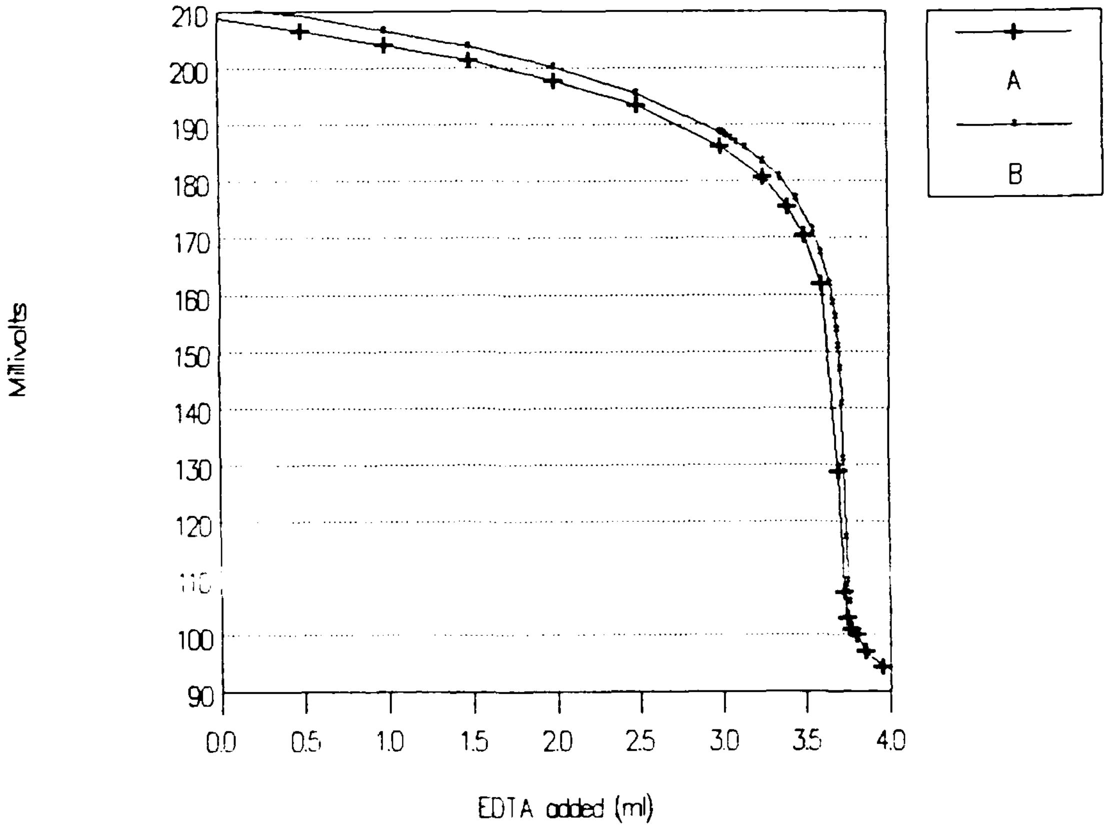


Figure 3.2 EDTA titration curves

3.3 **Experimental Methods**

3.3.1 XAD-8 Isolation

The procedure of Thurman and Malcolm (1981) for isolating humic substances was used with some modifications. The apparatus consisted of a 2-ft long, 3-inch diameter column filled a quarter from the bottom with XAD-8 resin. A separating funnel served as a reservoir for the groundwater feed and connected to the column with 1/4-inch tygon tubing along with a stopcock for flow control. Procedures used follow:

a) Column prepared with three liters of Milli-Q water passed through until the outflow pH was between 5 and 6.

b) 600 mls of pH 2 HNO_3 solution passed through the column.

c) 0.45 μm-filtered groundwater at pH 2 adjusted with HNO_3 passed through the column at an outflow rate of 25 $\pm$ 2 ml/min.

d) 250 mls of pH 2 HNO_3 solution passed through until one inch of water remained in the resin.

e) 0.1 N NaOH passed through until the outflow absorbance equaled the inflow with the eluate of humic acid collected.

f) A hydrogen cation exchange resin was added to the collected eluate in a batch mode and stirred for 1.5 hours. The amount of resin added was determined with the following equations (Waterbury, 1990):

$$(\text{ml of eluate})\ (0.1\ N\ NaOH) = (\text{meq of active material})$$

$$\frac{(\text{meq of active material})}{(5.1\ \text{meq / dry g resin})} = (\text{g of resin added}) \quad (22)$$

g) The resin and eluate solution passed through a 0.45 μm filter membrane to separate the resin from the dissolved humic substance.

The OCGW humic concentrate was diluted with Milli-Q then stored at its natural DOC of 5.66 mg/L. BA humic concentrate was stored in its concentrated form with a DOC of 50.2 mg/L and later diluted with Milli-Q for the titrations.

3.3.2 Titration Apparatus

Potentiometric and complexometric titrations for the model compounds, BA groundwater, and mixtures of model compounds were performed in 400-ml, polypropylene, jacketed beakers (see Figure 3.3). Titrations for the OCGW were performed in 150-ml, glass, jacketed beakers with temperatures controlled by recirculating water to 23° C. Titrations in polypropylene beakers were performed at room temperature (23° C ± 2). The apparatus for titrating the model compounds and BA groundwater was continually updated through this research project. Initial experiments were conducted with a Fisher Accumet 925 pH meter. A Fisher 753 electrode switch was then added to allow the measuring of

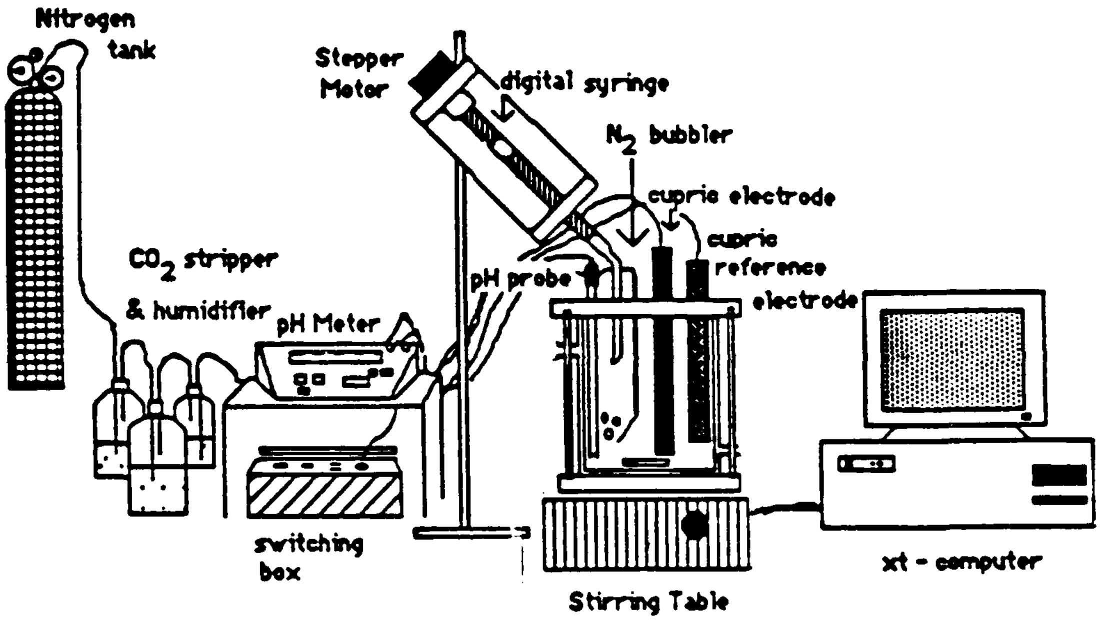


Figure 3.3 Titration apparatus for model compounds and BA groundwater (after Waterbury, 1990)

both pH and free copper. Finally, a Fisher Accumet 950 pH/ion meter replaced both the pH meter and the electrode switch. Measurements were taken with a Radiometer America combination pH electrode and an Orion double junction reference and cupric electrode. A VWR model 310 magnetic stirrer ensured adequate mixing. A nitrogen atmosphere was used in all titrations. N_2 gas was washed by bubbling through solutions of 2.0 N NaOH and Milli-Q water. An autoburette was used to add aliquots of acid or copper. The autoburette consisted of a Superior Electric Slo-syn synchronous/stepping motor, type MO61-FC02, equipped with a Breg autoburette P/N JJ-9. The motor was controlled by an IBM-compatible microcomputer through a AST Research CK 7260 multi I/O, a John Bell 86-108A Universal Parallel Interface, and a Rogers Lab R2D23 dual axis stepper motor driver board. The experimental set-up for OCGW titrations also included a Haake KT2 water temperature recirculator. A BASIC software program (see Appendix D) allowed parameter controls by the user and provided both hardcopy and printed data. For each aliquot added; time, millivolt or pH, and the volume of titrant was recorded.

Prior to starting a titration, the samples were reduced to pH 3 with HNO_3 and then purged with N_2 gas for at least 4 hours to remove CO_2 gas. $NaNO_3$ was added to the solutions to adjust the ionic strength to 10 mM.

3.3.3 Potentiometric Titrations

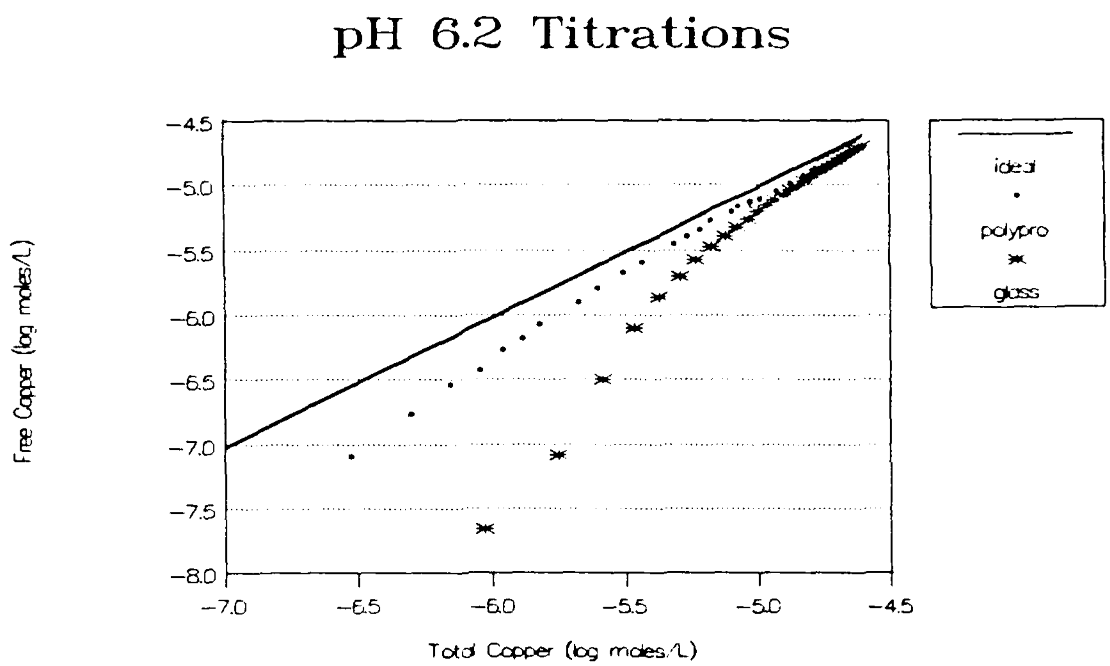
Potentiometric titrations were performed on catechol, glycine, phthalic, salicylic, and the XAD-8 humic acid fractions of OCGW and BA. Replicates were only performed for glycine. The XAD-8 isolates were titrated at a DOC of 5.66 mg/L for OCGW and 12.5 mg/L for BA (a 3:1 dilution of the XAD-8 eluate). Titrations began at pH 3 and ended at pH 10. Carboxylic acidities were determined from the operational definition by Thurman (1985) with Milli-Q water corrections.

3.3.4 Complexometric Titrations

All complexometric titrations were conducted in the dark to prevent light interferences to the cupric electrode. A 200-ml volume of the samples at varying compound concentrations was used for the titrations. Concentrations from 1×10^{-4} M to 5×10^{-4} M was required of MES to maintain the pH at 6.2 ± 0.1. Titrations performed at pH 7.5 needed 0.5 to 5 mM HEPES to maintain the pH at 7.5 ± 0.01. DOCs of the OCGW samples were the same as the potentiometric titrations. For BA the DOC was reduced by 2.5 times to 5.02 mg/L to get complexation within the range of the copper probe. Aliquots of 1 mM copper were titrated and allowed to equilibrate for 10 minutes. Complexometric titrations for BA, however, were allowed to equilibrate for up to 30 minutes towards the end of the titrations. Replicates were again only performed on glycine at pH 6.2 and pH 7.5.

Prior to determining the binding effects of the compounds, Milli-Q blanks were titrated to show any sorption on the titrating vessels, complexation by the Milli-Q water source and buffers, and error in measurements. Shown in Figure 3.4 are Milli-Q titrations compared to an ideal blank of ultrapure water with no carbonate species at an ionic strength of 10 mM modeled with TITRATOR using Cu-OH constants from Paulson and Kester (1980). MES buffer concentration at pH 6.2 was 0.1 mM, and HEPES buffer at pH 7.5 was 5 mM. The loss in linearity of the copper probe can be seen on the curves.

OCGW XAD-8 was titrated under temperature-controlled conditions in a glass beaker; whereas, BA XAD-8 was titrated at room temperature in a polypropylene beaker.



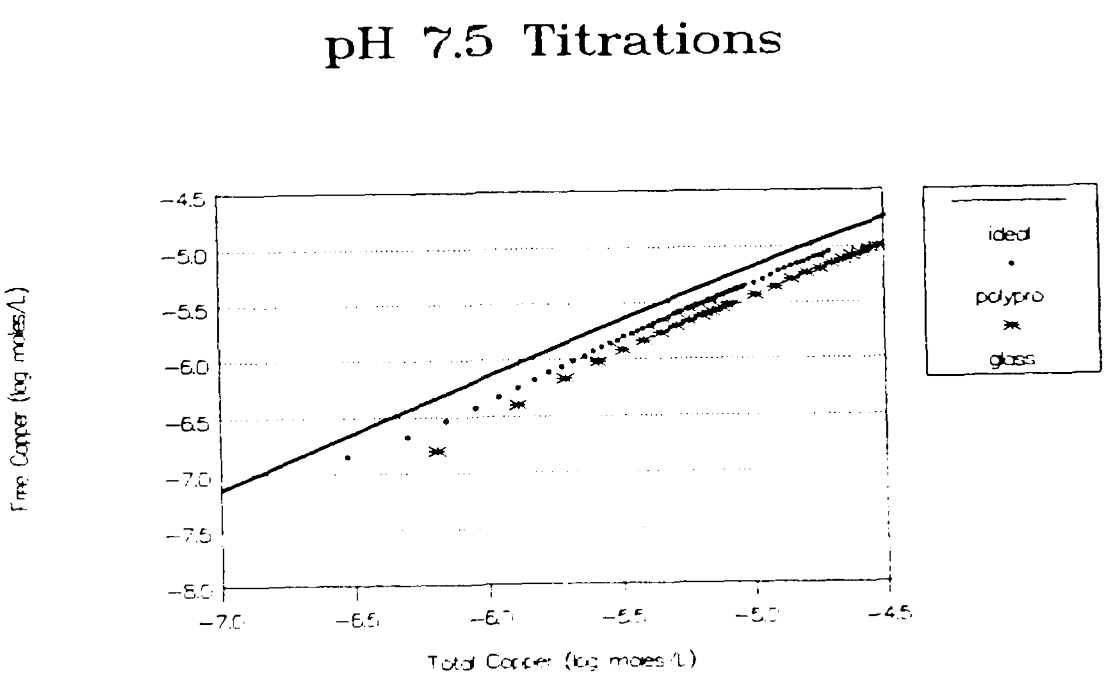


Figure 3.4 Milli-Q complexometric titrations

3.4 **Data Analysis**

Dissociation and binding constants from the titrations were verified with published constants using an interactive computer program called TITRATOR (Cabaniss, 1987). Potentiometric titrations were fitted using an iterative process with TITRATOR. Values for the model compound concentrations were based on carboxylic content, phenolic content, and nitrogen content. Complexometric data of the natural sources were initially fitted with a non-linear squares regression, statistical package (SAS, 1979) using an approach similar to Cabaniss and Shuman (1988a). Assumptions for which ligand species dominated at a certain pH were based on pK_a values. Once optimum fitting parameters were calculated, adjustments to the parameters were made using TITRATOR. Adjustments were only required for catechol and glycine (see Table 3.2).

The fitting of the complexometric data first included fitting each of the model compounds with SAS to identify the ligand and concentrations to use for further modeling. Two of the model compounds (either catechol, phthalic or salicylic acid) were then fitted to the data, and then those concentrations were used for a 3-ligand fit to the data with a set concentration of glycine based on assumed values of nitrogen content.

Table 3.2 SAS equations and adjusted binding constants

Compound	K^*	Adjusted K
catechol:		
$[CuL_{Cat}] = \dfrac{[L_T]\ [Cu]\ K_{CuH}}{\{H\}^2 + [Cu]\ K_{Cu}}$	-8.345	-7.96
glycine:		
$[CuL_{Gly}] = \dfrac{[L_T]\ [Cu]\ K_{CuH}}{\{H\} + [Cu]\ K_{CuH}}$	-1.3	-1.24
phthalic acid:		
$[CuL_{Phth}] = \dfrac{[L_T]\ [Cu]\ K_{Cu}}{1 + [Cu]\ K_{Cu}}$	4.0	----
salicylic acid:		
$[CuL_{Sal}] = \dfrac{[L_T]\ [Cu]\ K_{CuH}}{\{H\} + [Cu]\ K_{CuH}}$	-2.45	----

(after Cabaniss and Shuman, 1988a)
* from published constants (see Table 2.5)

CHAPTER 4

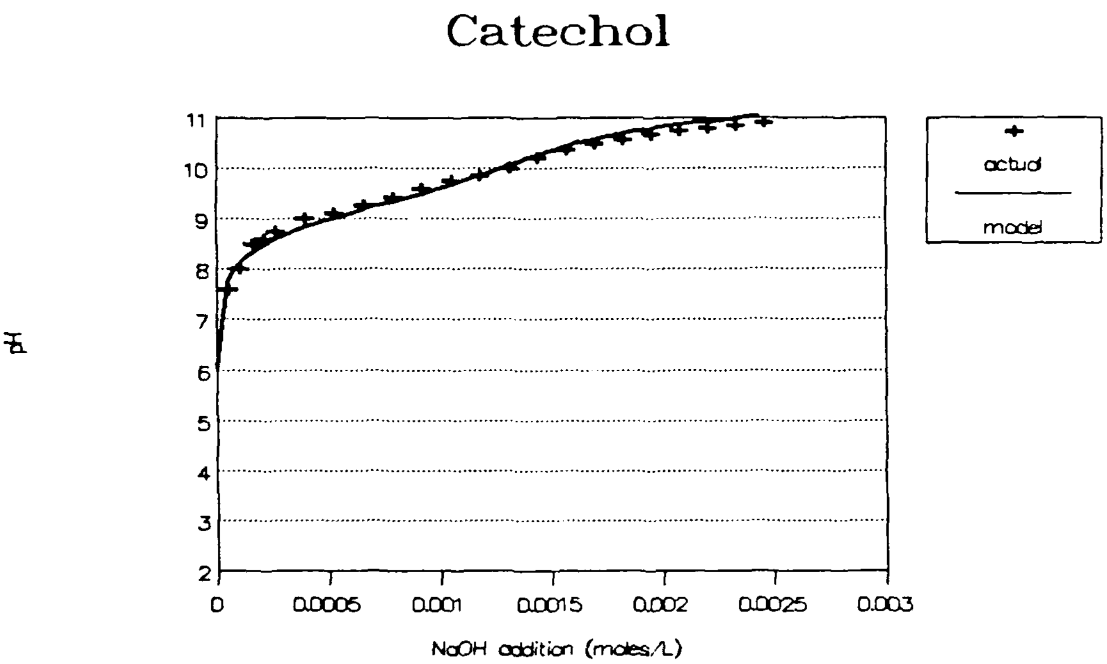
RESULTS AND MODELING

4.1 Single Model Compound Titrations

Potentiometric and complexometric titrations of catechol, glycine, phthalic acid, and salicylic acid were done to verify dissociation and binding constants with the published values. The replicates performed on glycine, with error bars for the complexometric titrations, are included in the figures. Titration data are included in Appendix A.

4.1.1 Potentiometric Titrations

Potentiometric titrations performed on each model compound and the model fits are shown in Figures 4.1a and 4.1b. With the exception of glycine, all of the model compounds were titrated without adjusting the pH to 3. Figure 4.2 shows potentiometric titrations of all the model compounds.



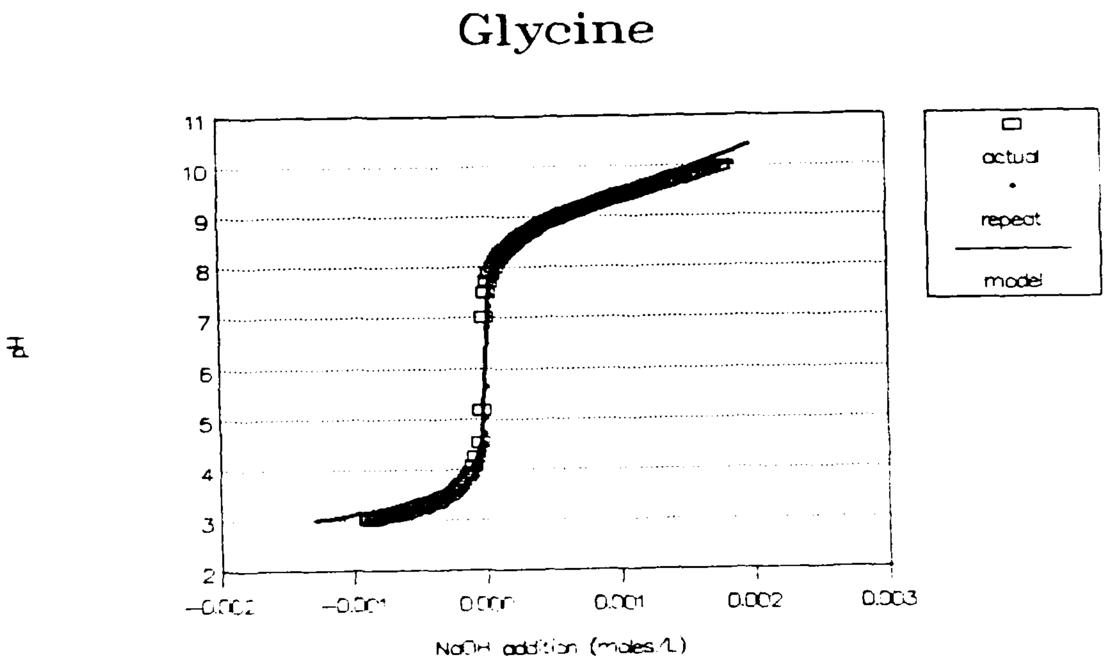
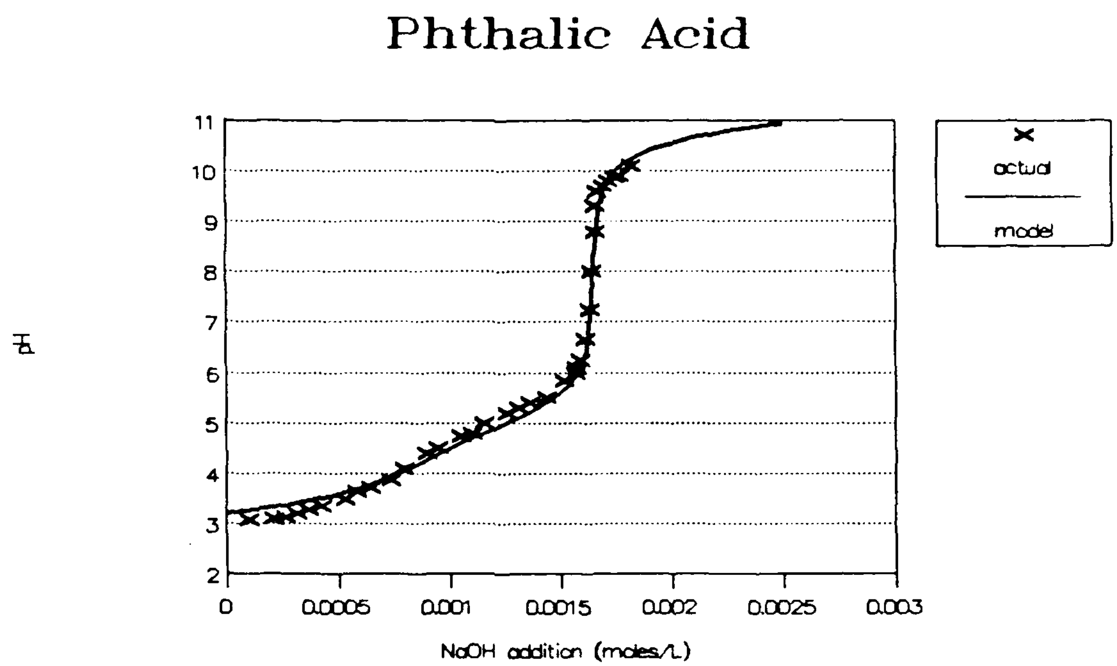


Figure 4.1a Potentiometric titration of model compounds - catechol (1.37×10^{-3} M) and glycine (2.0×10^{-3} M



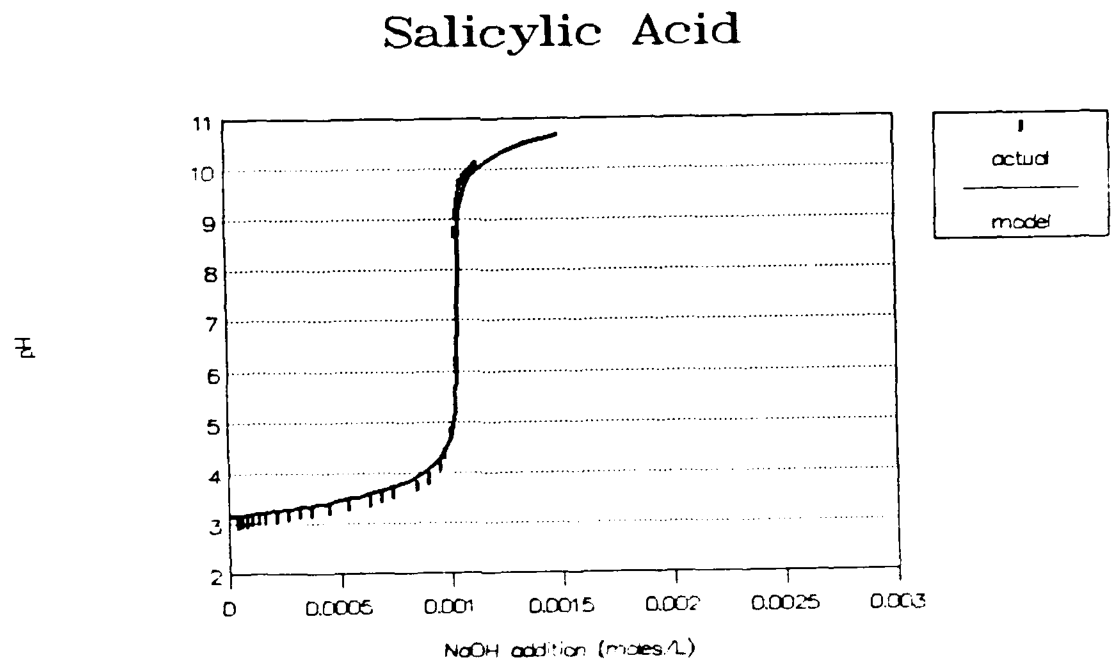


Figure 4.1b Potentiometric titration of model compounds - phthalic acid (8.25 X 10^{-4} M) and salicylic acid (1.04 X 10^{-3} M)

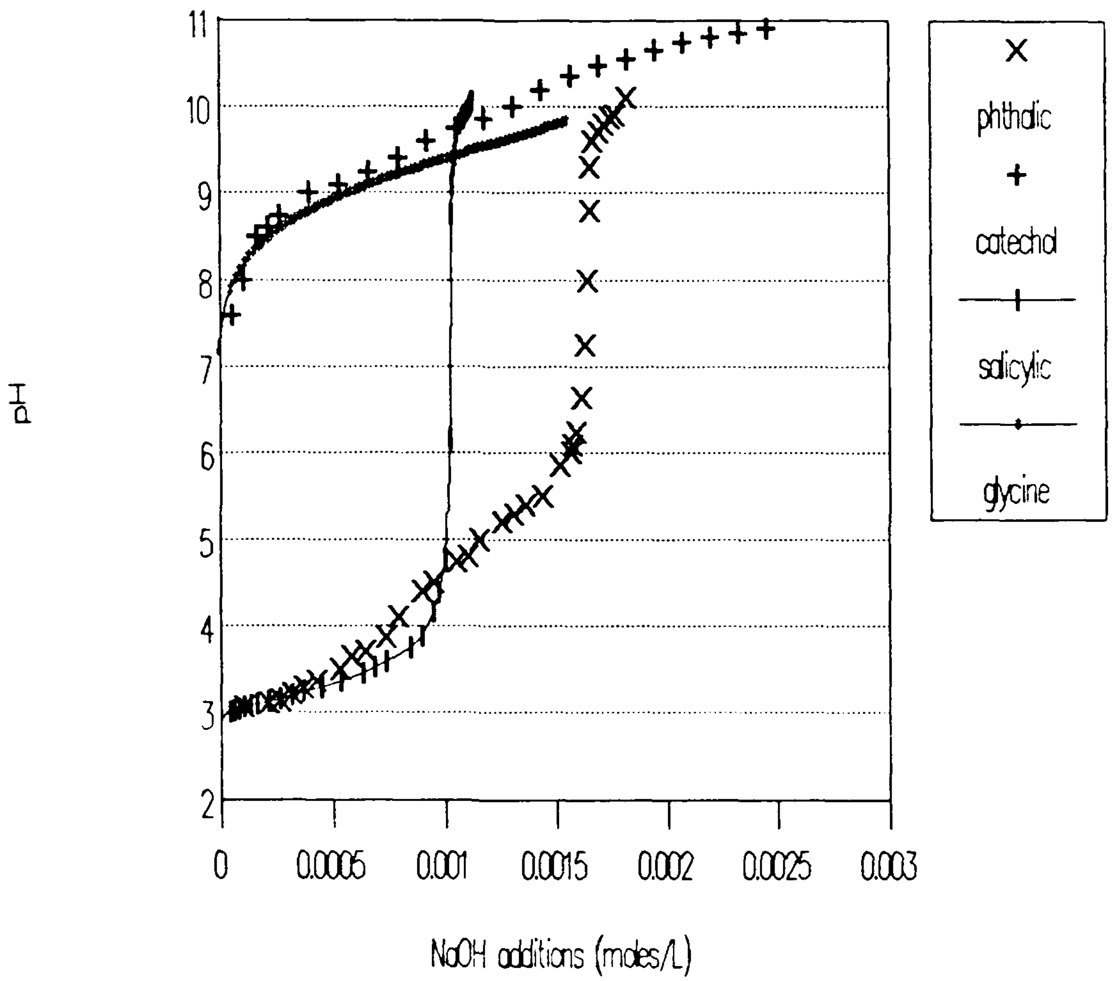


Figure 4.2 All model compounds - potentiometric titrations

4.1.2 Complexometric Titrations

Determining binding constants for the model compounds used required more careful attention to changes caused by temperature and ionic strength. Calculated experimental values per Neshkova and Sheytanov (1985) and temperature and ionic corrections per Smith and Martell (1975) are shown in Table 4.1.

Experimental binding values calculated and summarized on Table 4.1 do not reflect all the binding that occurs. Validating binding constants was accomplished by comparing the actual experimental curves with model curves based on published values (see Table 2.5) using TITRATOR. Figures 4.3a, 4.3b and 4.3c show a good fit for the experimental and model curves of catechol, glycine and phthalic. For salicylic, the experimental curves did not fit with model curves (see Figure 4.3d). In this case, the binding constants were determined and used for further modeling. Binding constants of B_1 and B_2 at 11.15 and 18.96, respectively, were used as opposed to published values of 10.80 and 18.45 (see Table 2.5). Replicates of glycine performed have the error bars shown in Figure 4.4. Values normalized to the total ligand concentrations (L_T) equal to one for all the model compounds are shown in Figure 4.5.

Table 4.1 Experimental constants

Experimental Values	Catechol (H_2L)	Glycine (HL)	Phthalic ($H_2 L$)	Salicylic ($H_2 L$)
		Model Compounds		
Potentiometric		same as published values (see Table 2.5)		
Complexometric (temp. °C, ionic strength)				
B_1 pH 6.2	13.59 (23,0.01)	8.40 (21,0.01) 8.42 (22,0.01)	4.02 (21,0.01)	10.52 (23,0.008)
B_1 pH 7.5	12.6 (21,0.011)	8.01 (23,0.008) 8.24 (21, .01)	4.14 (23,0.01)	11.18 (22,0.01)

$B_1 = ML/M \cdot L$

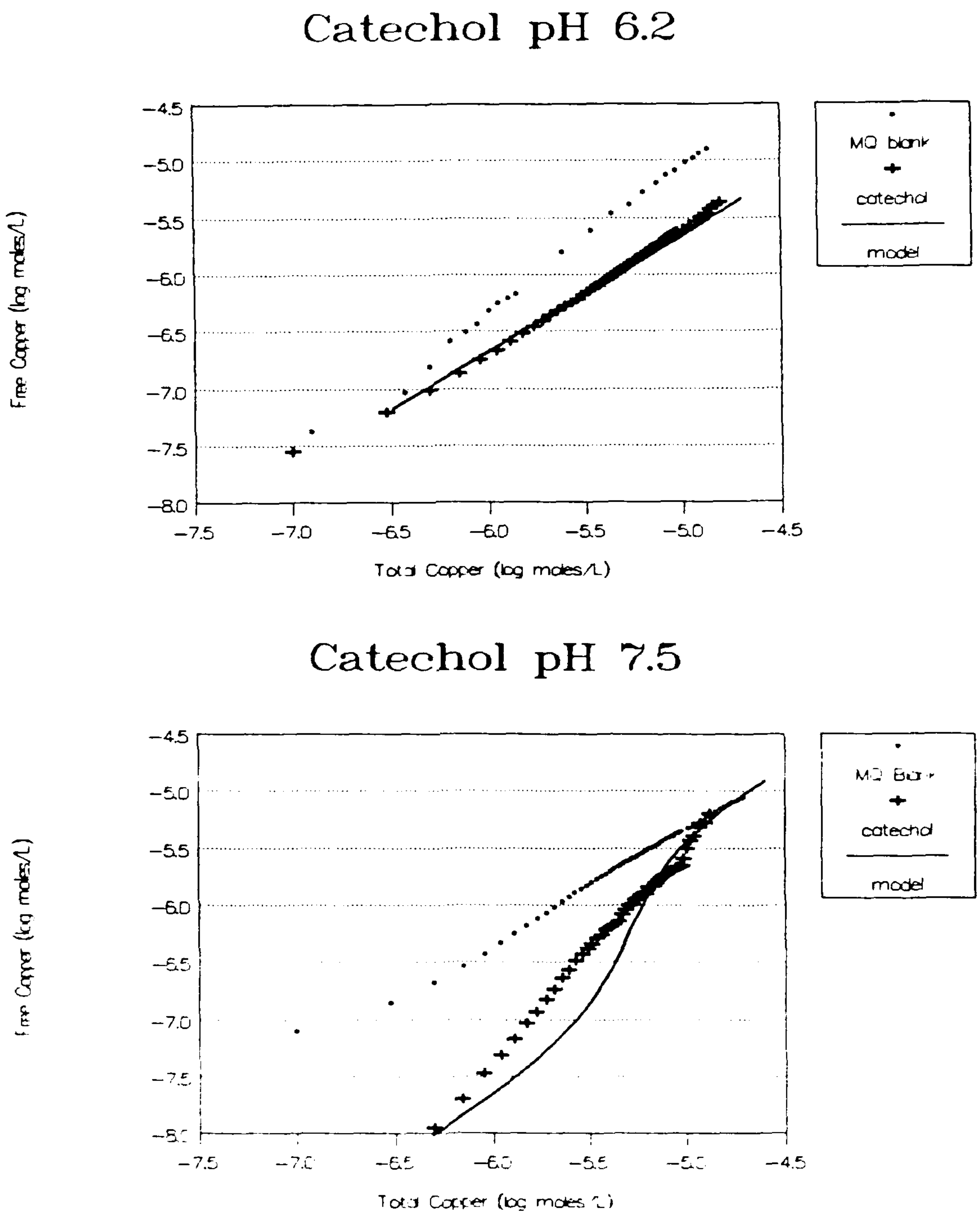
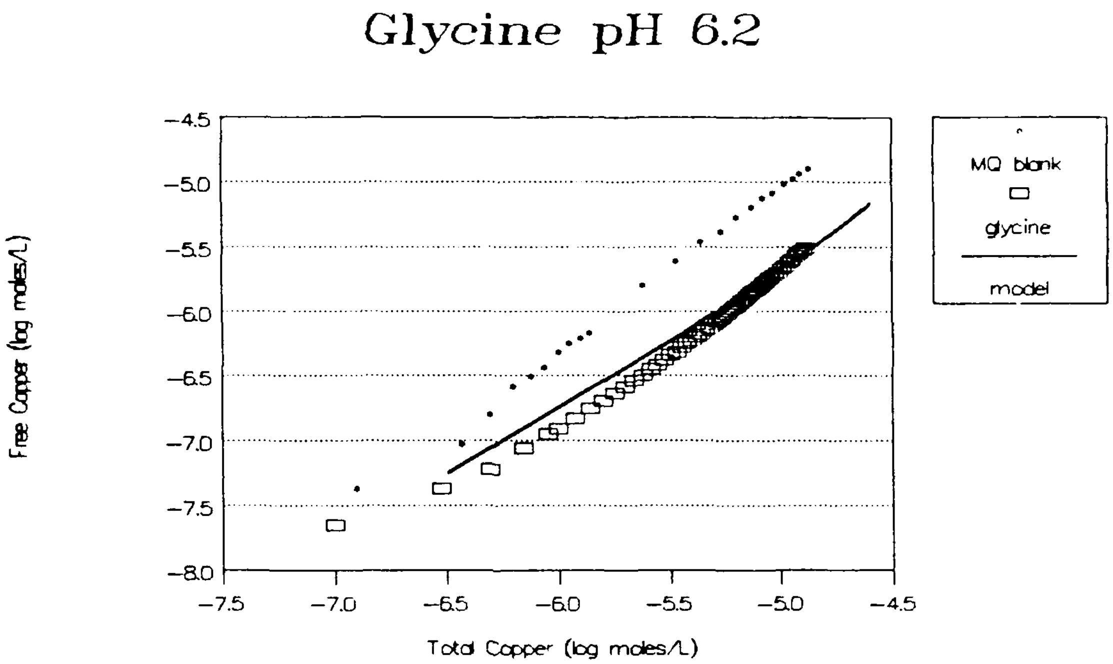


Figure 4.3a Model and experimental curve - catechol
At pH 6.2 - 1.36 X 10^{-4} M, 23° C, I=0.01
At pH 7.5 - 4.99 X 10^{-6} M, 21° C, I=0.01



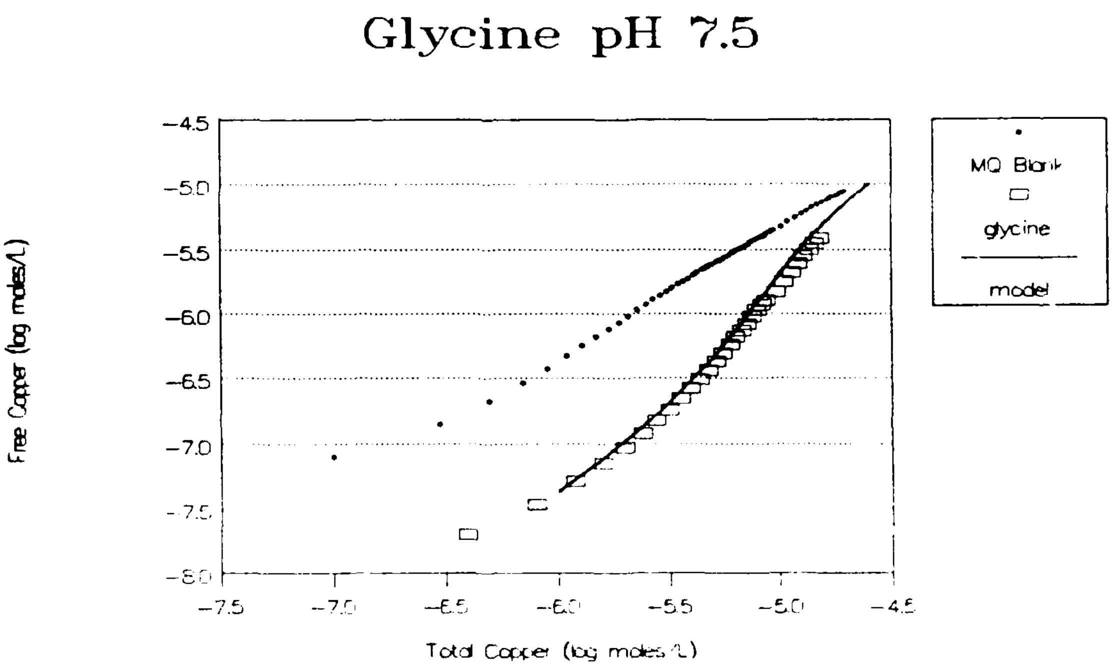
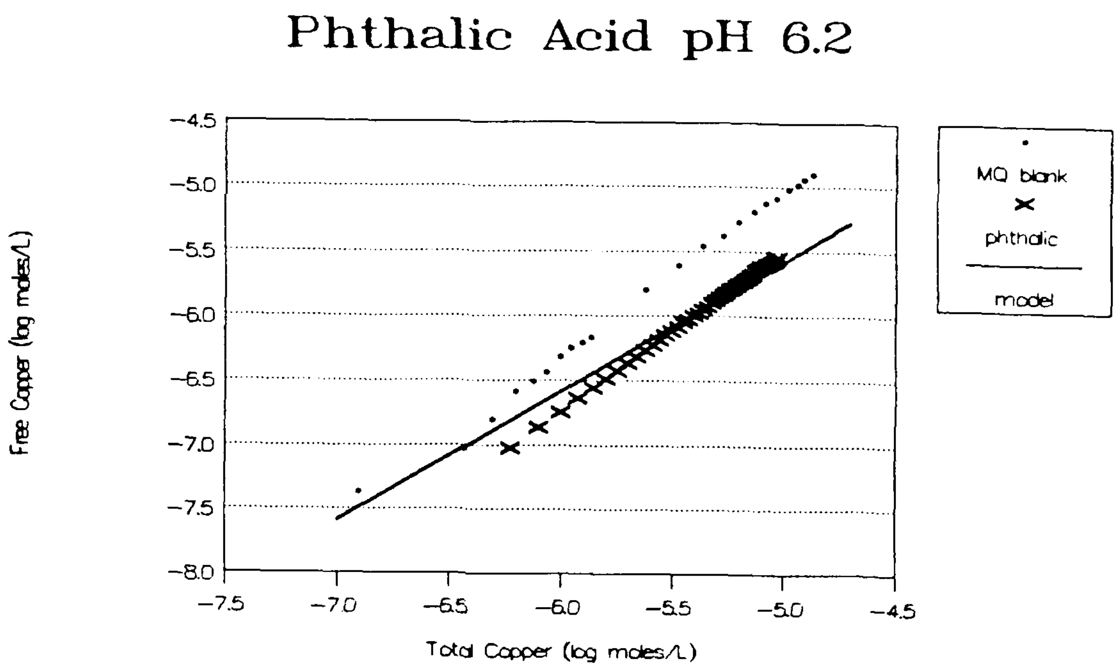


Figure 4.3b Model and experimental curve - glycine
At pH 6.2 - 1.0 X 10^{-4} M, 21° C, I=0.01
At pH 7.5 - 1.0 X 10^{-5} M, 23° C, I=0.008



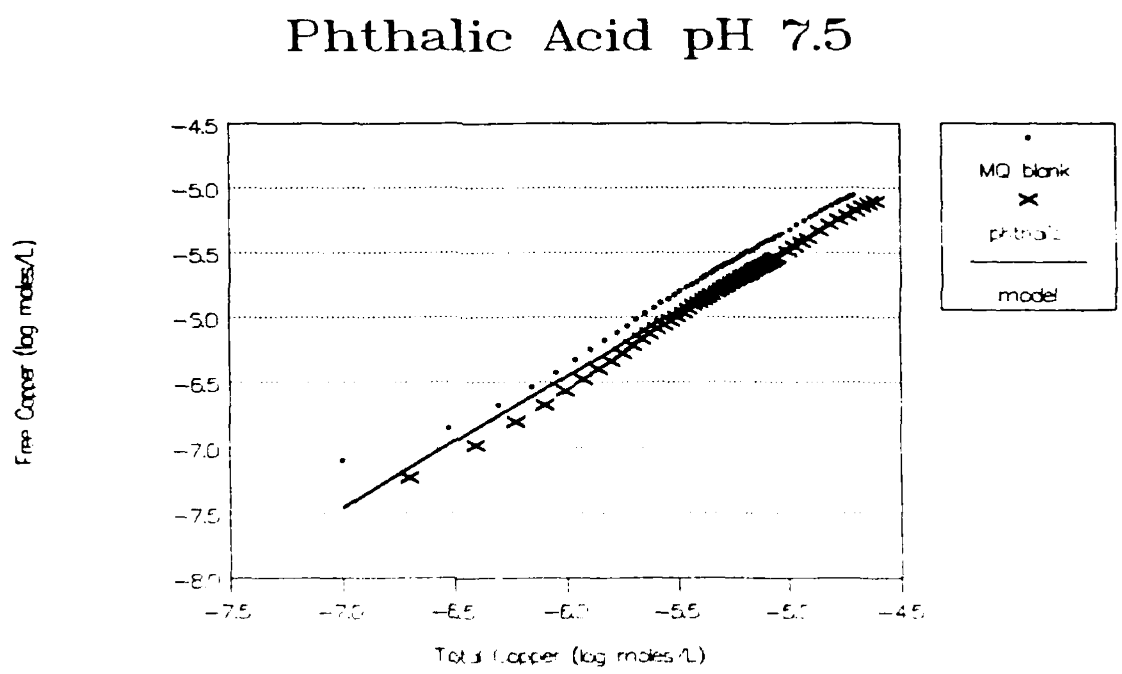


Figure 4.3c Model and experimental curve - phthalic acid
At pH 6.2 - 2.98 X 10^{-4} M, 21° C, I=0.01
At pH 7.5 - 1.5 X 10^{-5} M, 23° C, I=0.01

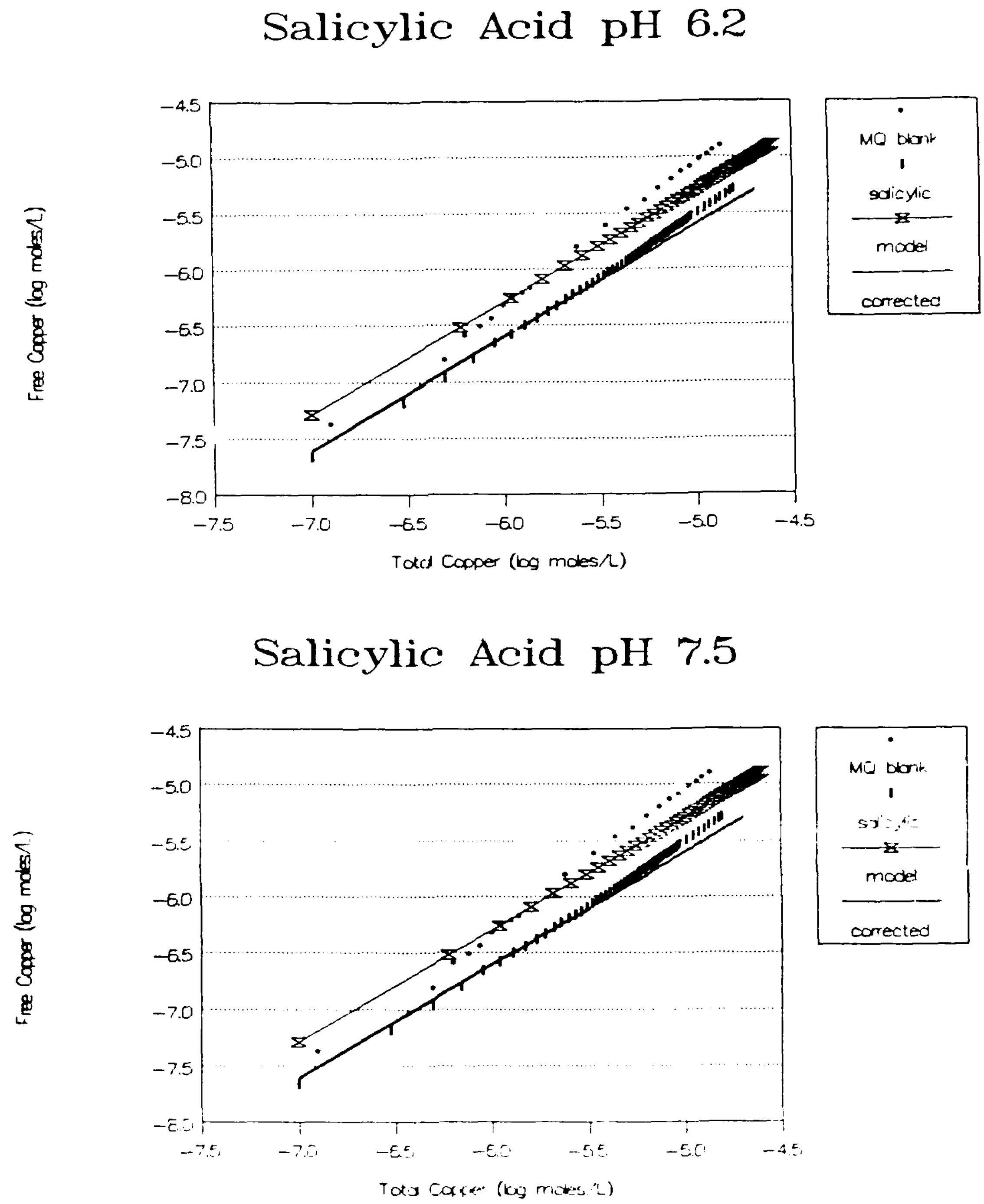


Figure 4.3d Model and experimental curve - salicylic acid
At pH 6.2 - 5.36 X 10^{-4} M, 23° C, I=0.008
At pH 7.5 - 1.13 X 10^{-4} M, 22° C, I=0.01

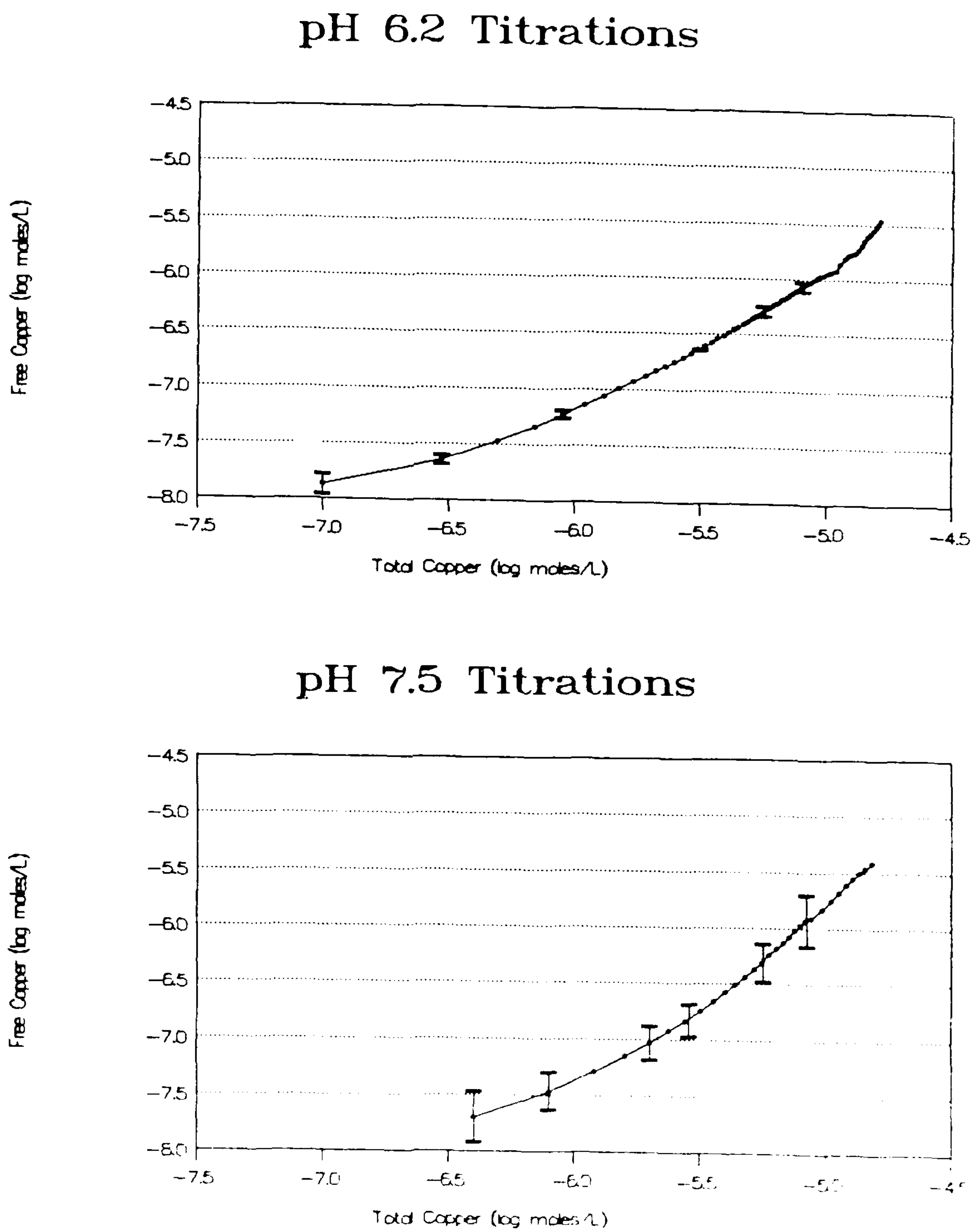
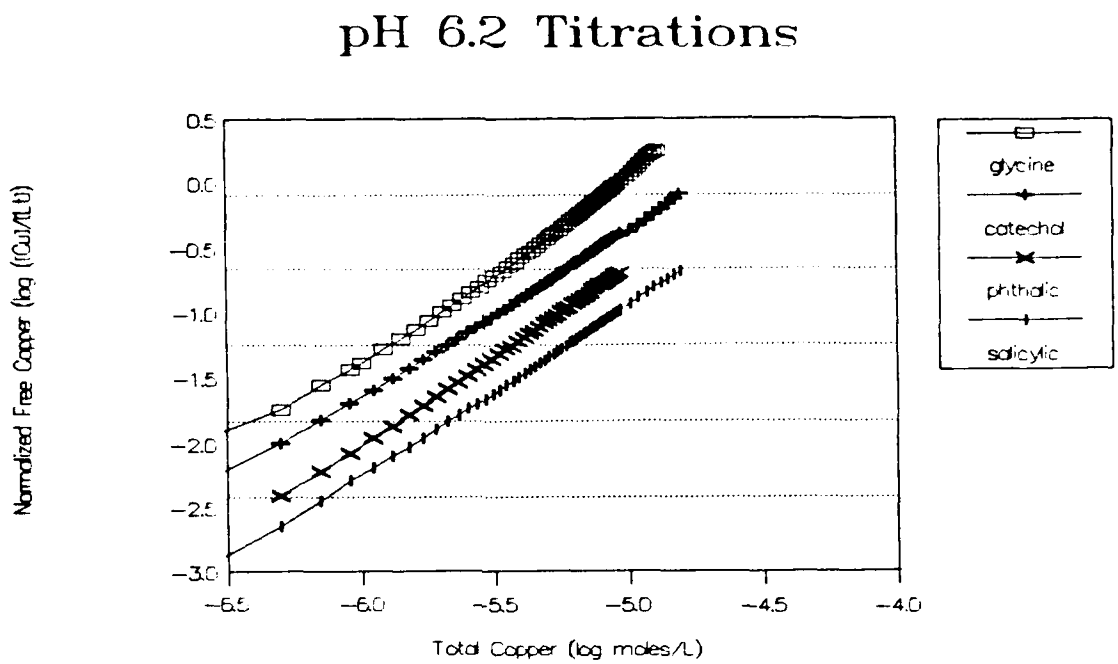


Figure 4.4 Glycine complexometric error bars



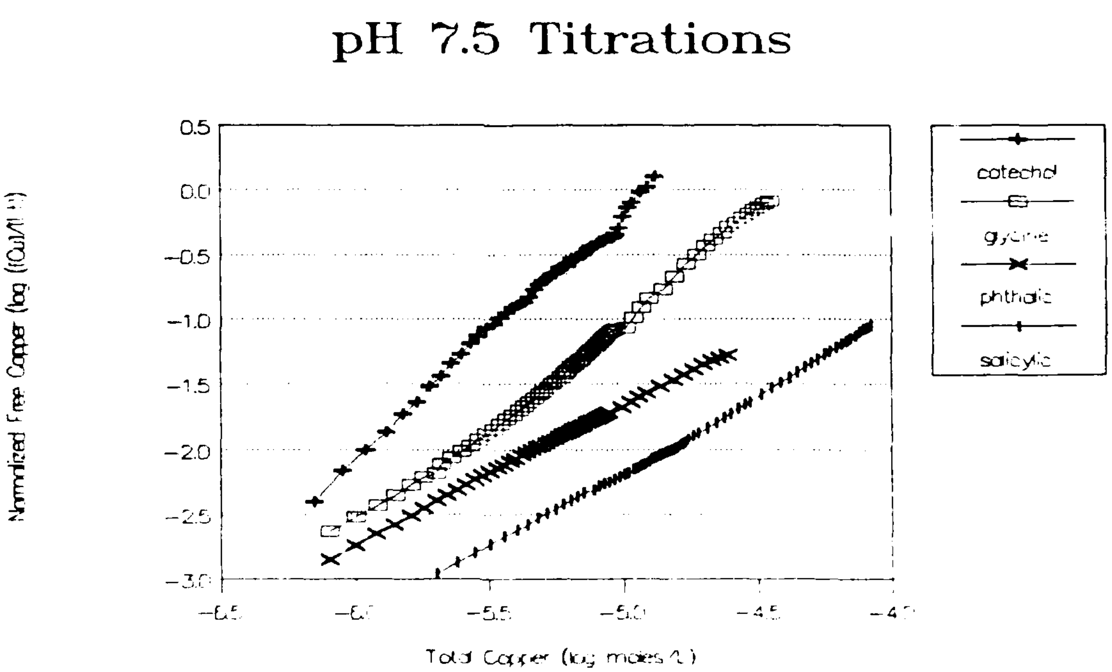


Figure 4.5 All model compounds - normalized to $[L_T] = 1$ complexometric titrations

4.3 Natural Sources and Model Compound Mixtures

The XAD-8 isolates of Orange County groundwater and Biscayne Aquifer groundwater were titrated potentiometrically and complexometrically (see Appendix C).

4.3.1 Potentiometric Modeling

Attempting to model each of the natural sources began by obtaining the carboxylic and phenolic acidities and DOC content of each of the solutions titrated (see Table 4.2). In keeping with the goal of using as much information about the chemical composition of the XAD-8 isolates to develop a model of a humic acid, concentrations for each of the single model compounds were calculated based on the following assumptions:

1) Glycine (NH_2CH_2COOH):

   [Gly] = nitrogen (N) concentration

2) Catechol ($C_6H_6O_2$):

   [Cat] = fraction (phenolic -OH concentration)/2

3) Salicylic acid ($C_7H_6O_3$):

   [Sal] = remaining phenolic -OH concentration

4) Phthalic acid ($C_8H_6O_4$):

   [Phth] = (Carboxylic conc. - [Gly] - [Sal])/2

Table 4.2 Titrated XAD-8 characteristics

Source and type	DOC (mg/L)	Carboxylic Acidity (meq/g-C)	Phenolic* Acidity (meq/g-C)	Nitrogen* Content (mg/L)
OCGW XAD-8				
	5.66	19.5 ± 3.53[1]	3.9	0
BA XAD-8				
	12.55	11.79	2.5	0.11

* assumed per Thurman (1985)
[1] Waterbury (1990)

To verify that reasonable concentrations were calculated, elemental compositions were compared to the ranges of measured compositions from different water sources.

DOC and the carboxylic content were experimentally determined. Values for phenolic and nitrogen content, however, were assumed using typical ranges (Thurman, 1985). The fraction of phenolic content present as catechol was varied with assumption (2) to obtain a good fit.

OCGW fitting was first attempted with no glycine and a catechol fraction of 1/2 the phenolic -OH content of 2 meq/g-C at 2.83 X 10^{-5} M. Increasing the catechol fraction had the effect of fitting the upper portion of the titration curve better (the phenolic portion), but too high a fraction (greater than 7/8) increased the error in the lower portion of the potentiometric fit (the carboxylic portion). The optimum fraction for catechol was determined at 75 percent of the phenolic -OH content. Next, the phenolic content was increased to better fit the upper portion of the curve. With increasing phenolic -OH content the error was reduced in the upper portion of the curve. However, concentrations of greater than 10 meq/g-C were needed to reduce the error. Schnitzer (1978) suggested a value of 3.9 meq/g-C as more appropriate. The addition glycine had little effect improving the potentiometric fit; therefore, it was assumed that nitrogen concentration in the form of glycine was present at 0.005 mg/L. The effect of these changes are

shown in Figures 4.6a and 4.6b.

For BA groundwater, the process of obtaining a good fit to the potentiometric titration data was similar to that performed on OCGW. Results are shown in Figure 4.7 and Table 4.3. Since the addition of salicylic acid did not help the fit, all the phenolic content at 2.5 meq/g-C was attributed to catechol. For the concentration of glycine, two concentrations were investigated: a low value of 121 nM/mg (0.1 percent), representing the concentration of amino acids present in BA humic acid, and a high of 5.8 percent nitrogen (Thurman, 1985). A value in between these two ranges provided the best fit. Phenolic -OH content was assumed to be constant at 2.5 meq/g-C per Thurman (1985).

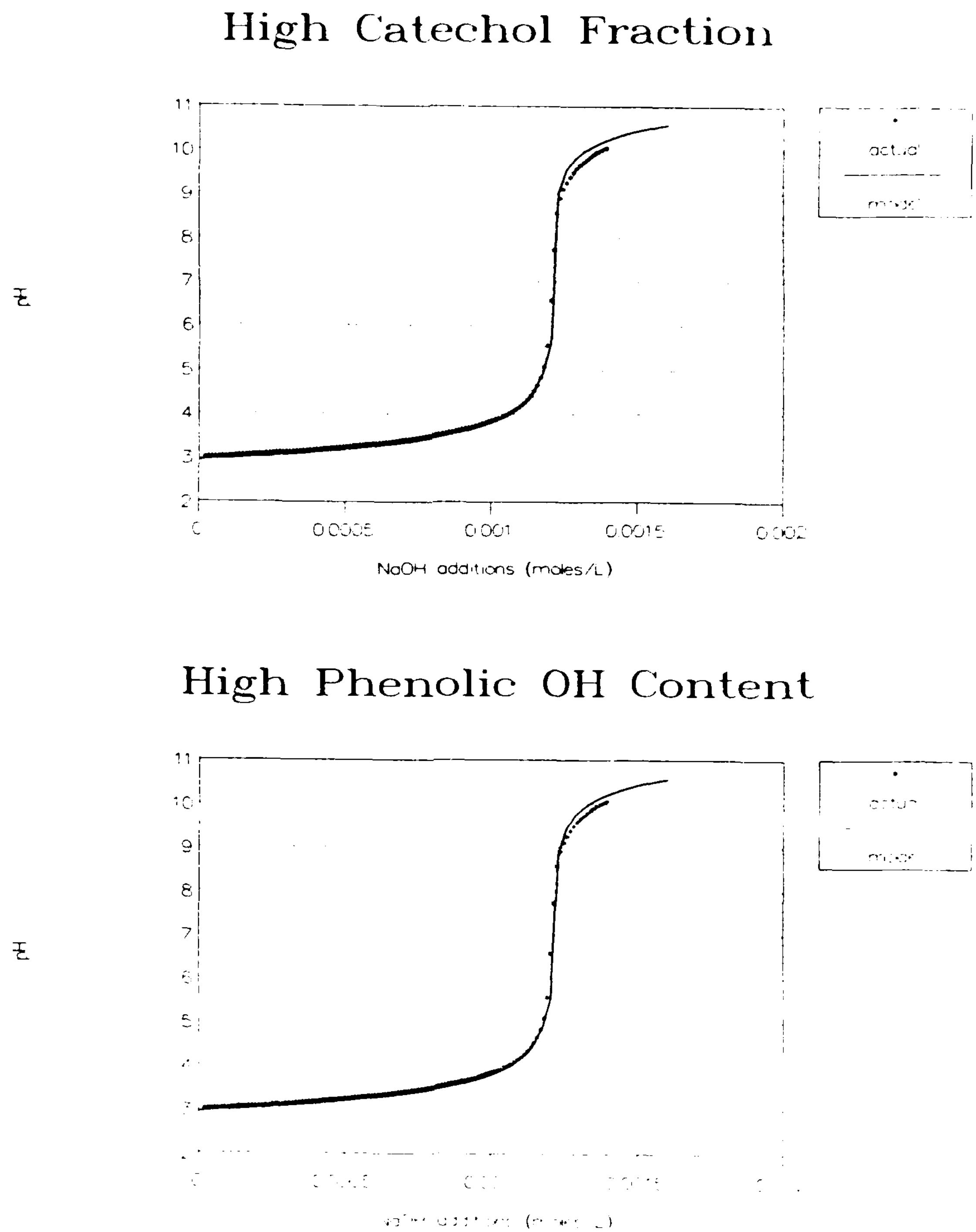
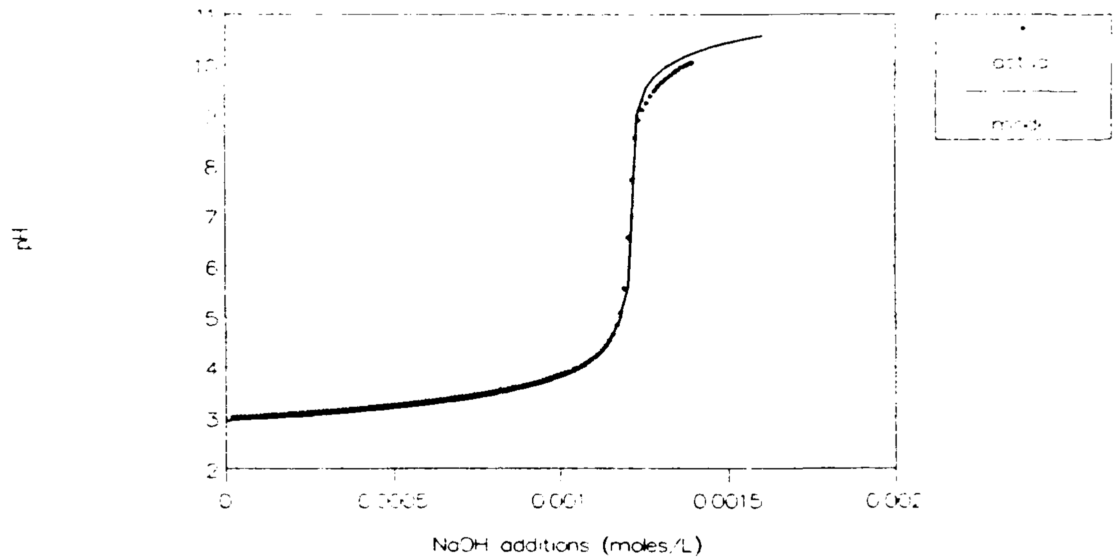


Figure 4.6a Potentiometric modeling of OCGW XAD-8 - catechol and phenolic effects (see text)

Nitrogen Addition



Final Potentiometric Fit

COOH=19.7meq/g-C;OH=3.9meq/g-C;Cat=3/4

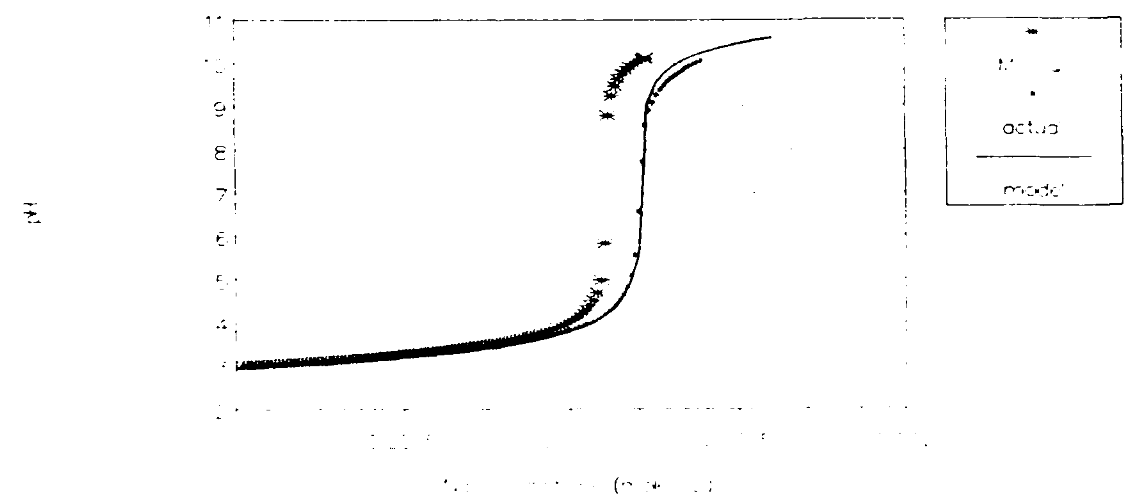


Figure 4.6b Potentiometric modeling of OCGW XAD-8 - nitrogen effects and final fitting (see text)

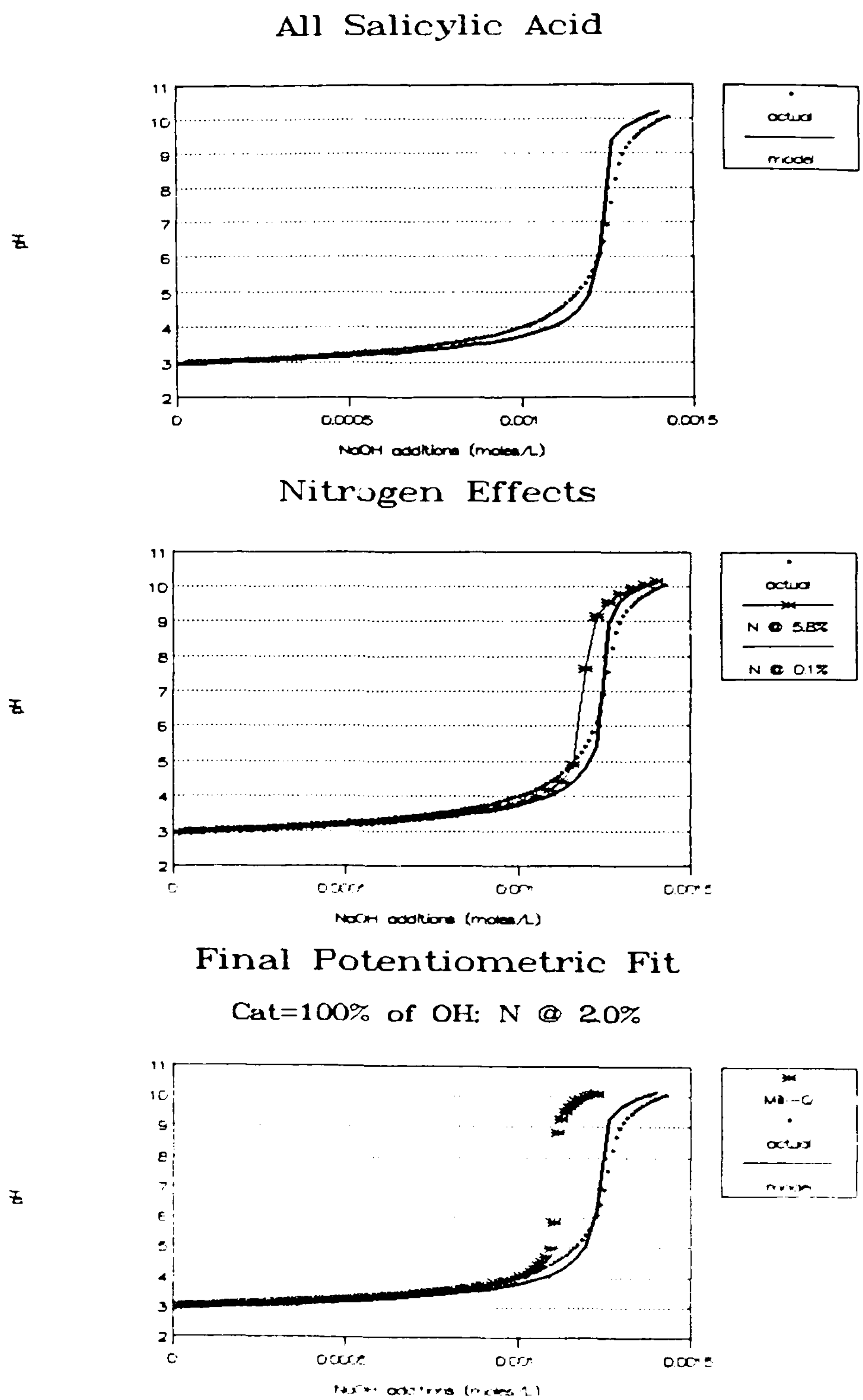


Figure 4.7 Potentiometric modeling of BA XAD-8 (see text)

Table 4.3 Assumed concentrations (pL) of model compounds

Source	Catechol	Glycine	Phthalic Acid	Salicylic Acid
OCGW	5.082	----	4.276	5.258
BA	4.804	4.699	4.194	----

4.3.2 Complexometric Modeling

Figures 4.8 and 4.9 show complexometric titration curves of OCGW XAD-8 and BA XAD-8, respectively. As shown on Figure 4.8, the pH 6.2 titration of OCGW showed problems with the Milli-Q blank titration. Values for the OCGW XAD-8 titration at pH 6.2 were corrected by subtracting the difference from the ideal Milli-Q titration and the actual from the XAD-8 titration. Since total copper concentrations for the data points did not match, a fitted model data set derived from Waterbury (1990) was used. No significant problem was noted for the other blank titrations of pH 6.2 in polypropylene an pH 7.5 in polypropylene or glass; therefore, the data was used without correcting for the blank (see Appendix C).

The same concentrations for the single model compounds were used to try to fit the complexometric curves. As shown on Figure 4.10a and 4.10b, there was not a good correspondence between fitted and actual values. Curve-fitting was attempted using SAS (see Appendix D). To an extent this effort was considered to be a divergence from the chemically approach being used.

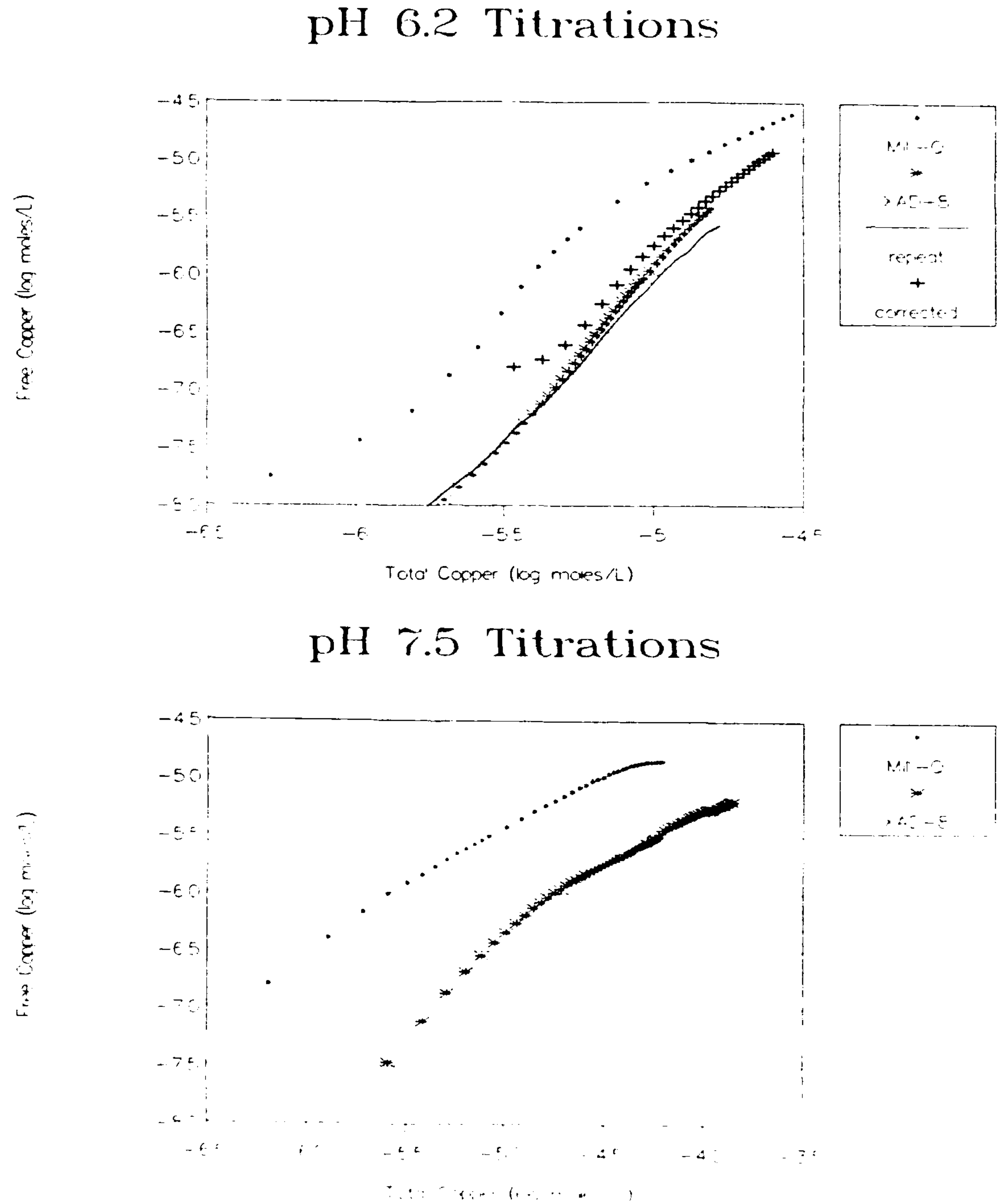


Figure 4.8 OCGW XAD-8 complexometric titrations

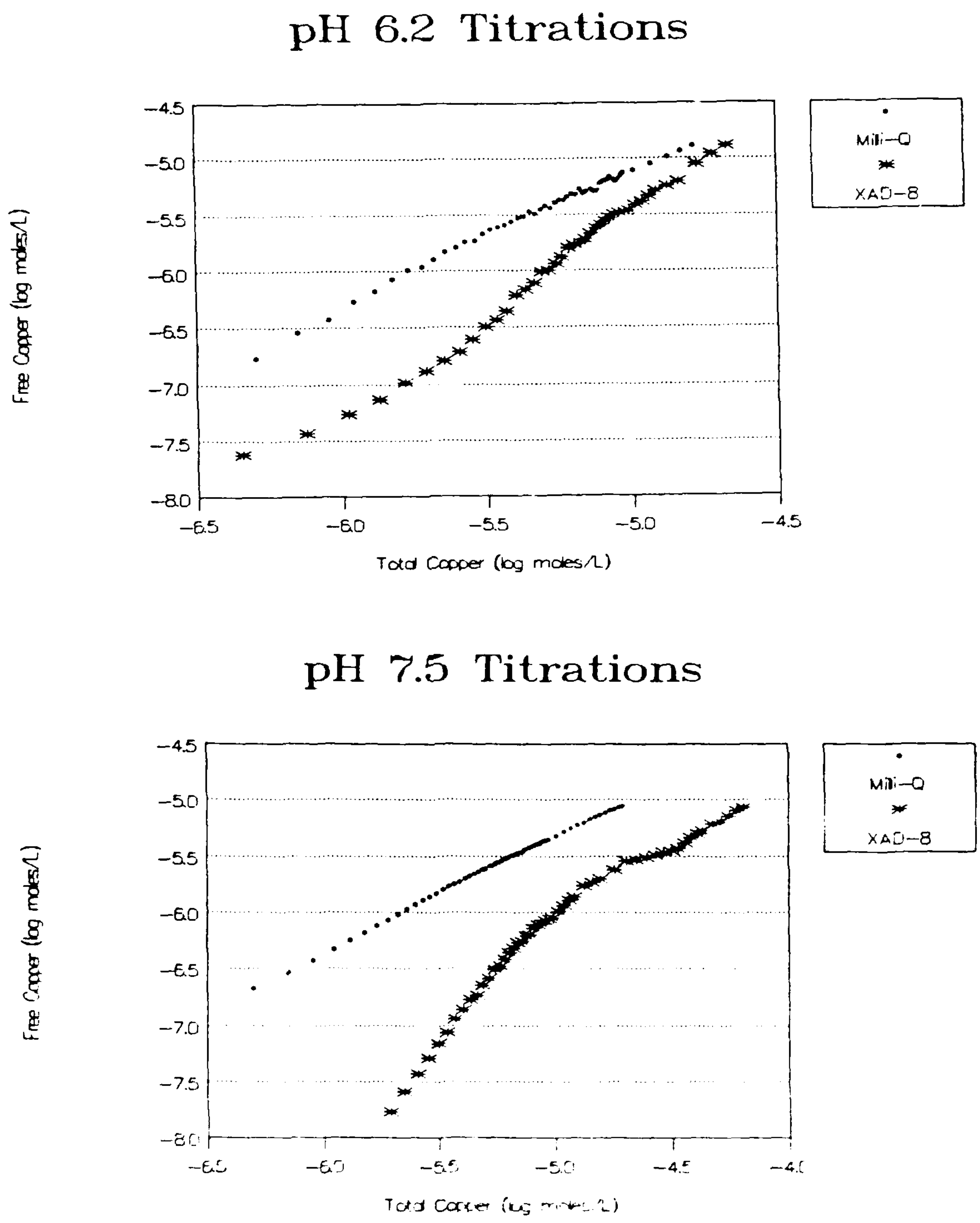
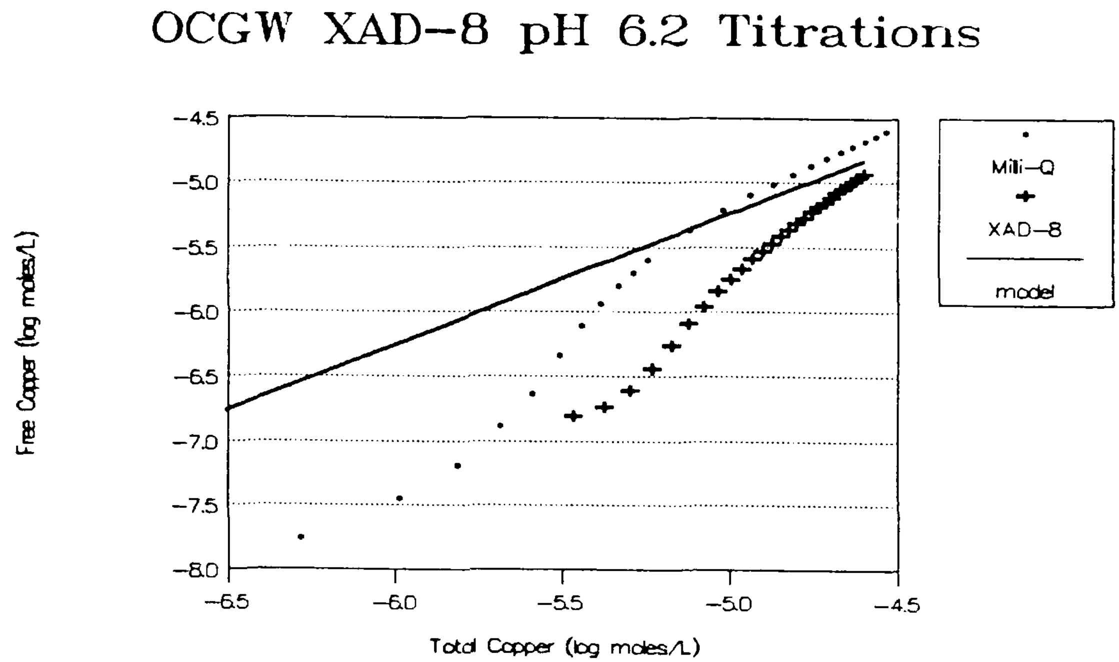


Figure 4.9 BA XAD-8 complexometric titrations



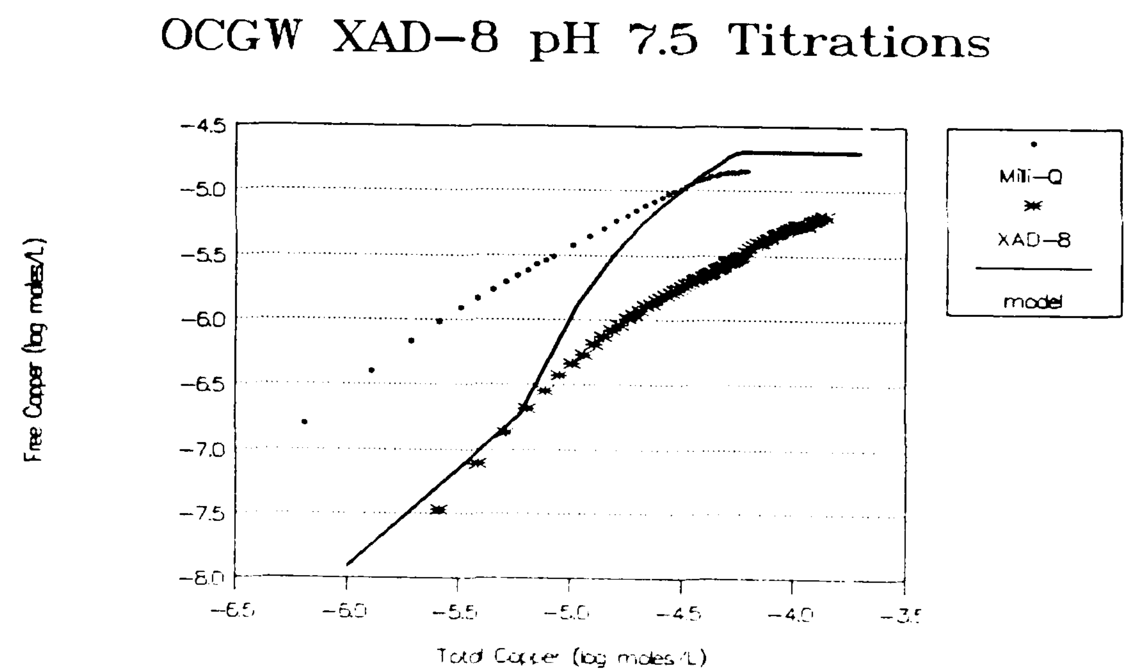
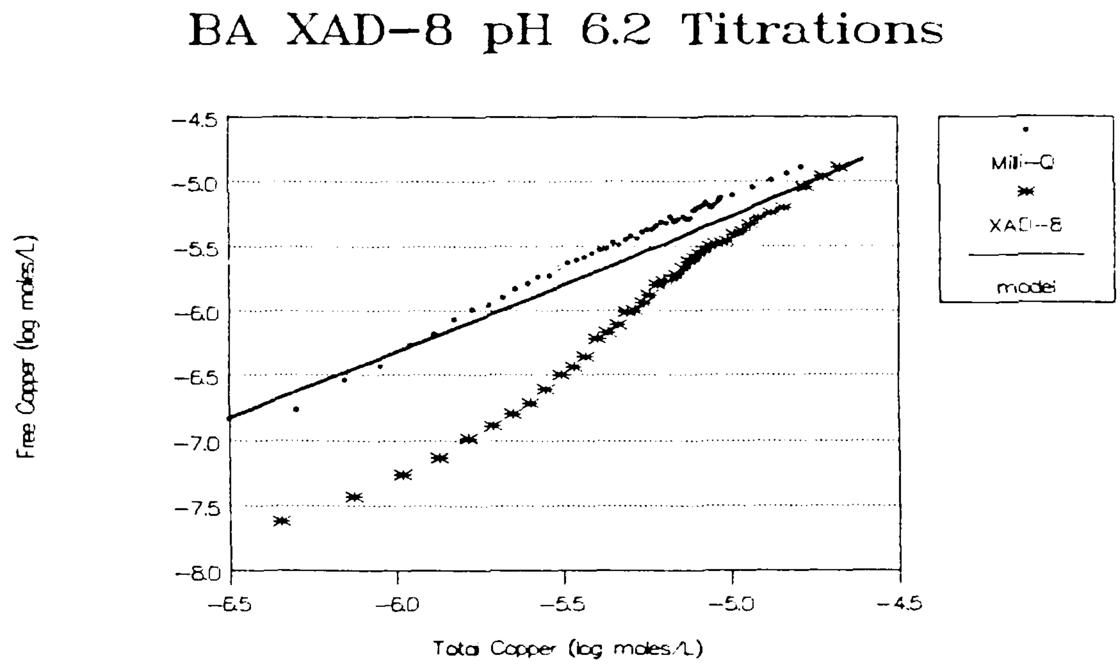


Figure 4.10a Complexometric curve fits with potentiometric mixture of model compounds - OCGW



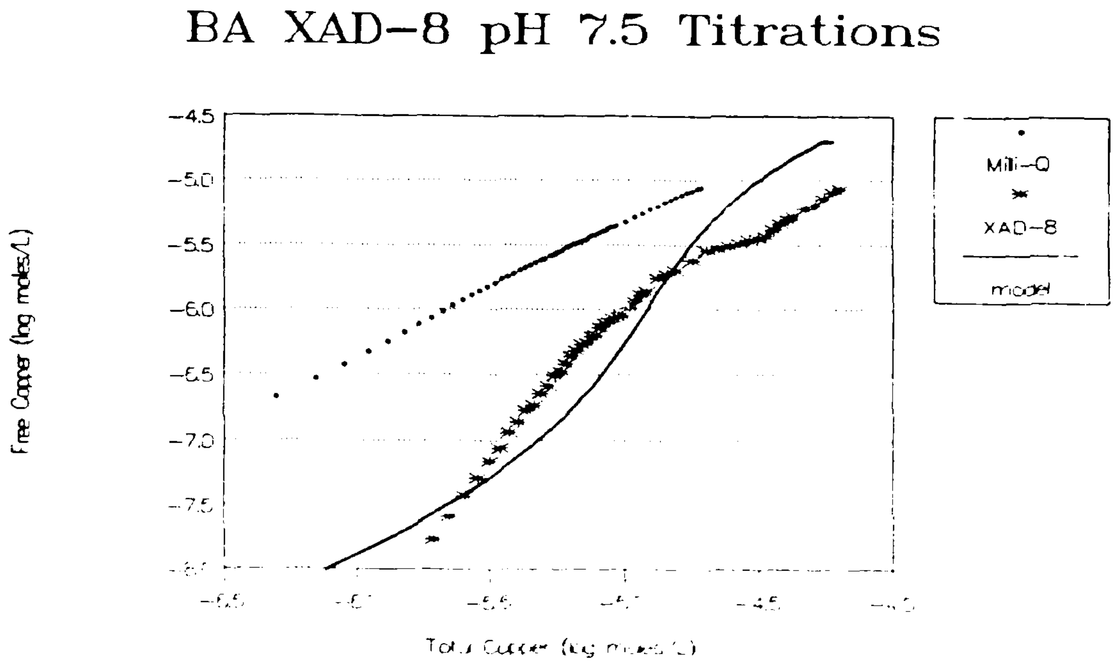
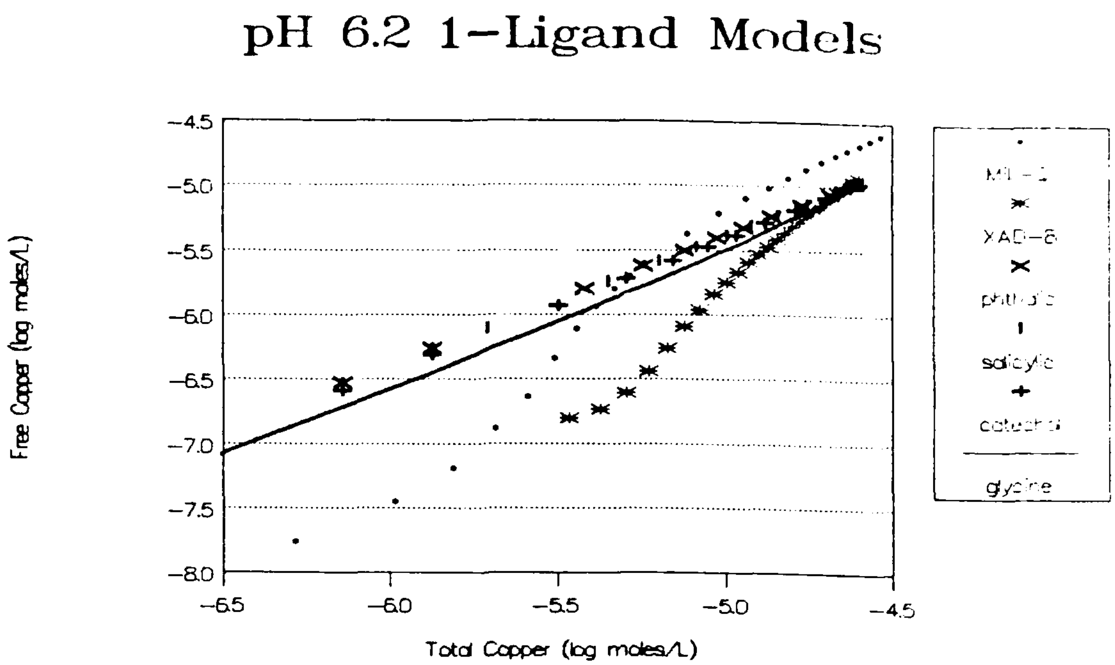


Figure 4.10b Complexometric curve fits with potentiometric mixture of model compounds - BA

For both XAD-8 isolates at pH 6.2, single-ligand concentrations of catechol, phthalic and salicylic acid were similar. Attempts at pH 7.5 had phthalic and salicylic acid with similar curves (see Figures 4.11 and 4.12). Since using both concentrations of salicylic acid and catechol would exceed the assumed phenolic -OH content, phthalic acid and catechol were chosen for the two-ligand fitting. After the concentrations of the two ligands were obtained on SAS, a reasonable guess was made for the three-ligand fitting. Results of the SAS outputs are shown on Table 4.4. Even though the best possible combination of elements was fitted with SAS, the elemental composition and acidities resulted in too high an estimate for carboxylic acidities (see Table 4.5) nor were the actual curves properly fitted with the sum of squares errors unacceptably large - OCGW pH 6.2 at 6.39×10^{-9}, OCGW pH 7.5 at 4.03×10^{-7}, BA pH 6.2 at 3.05×10^{-9}, and BA 7.5 at 2.97×10^{-8} (see Figure 4.13a and 4.13b).



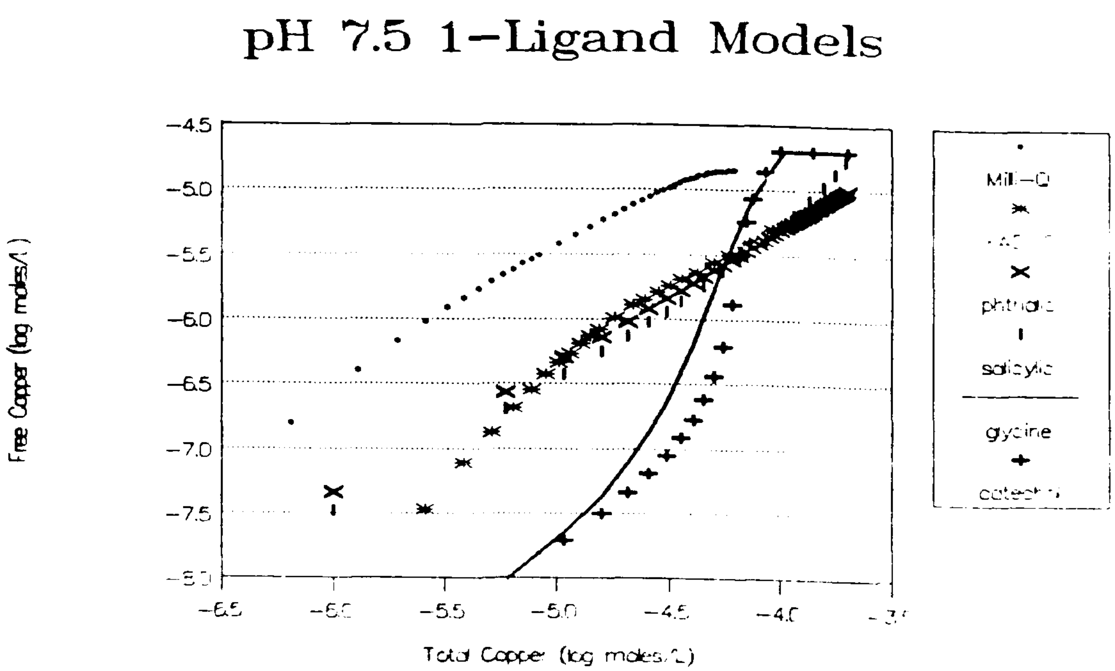
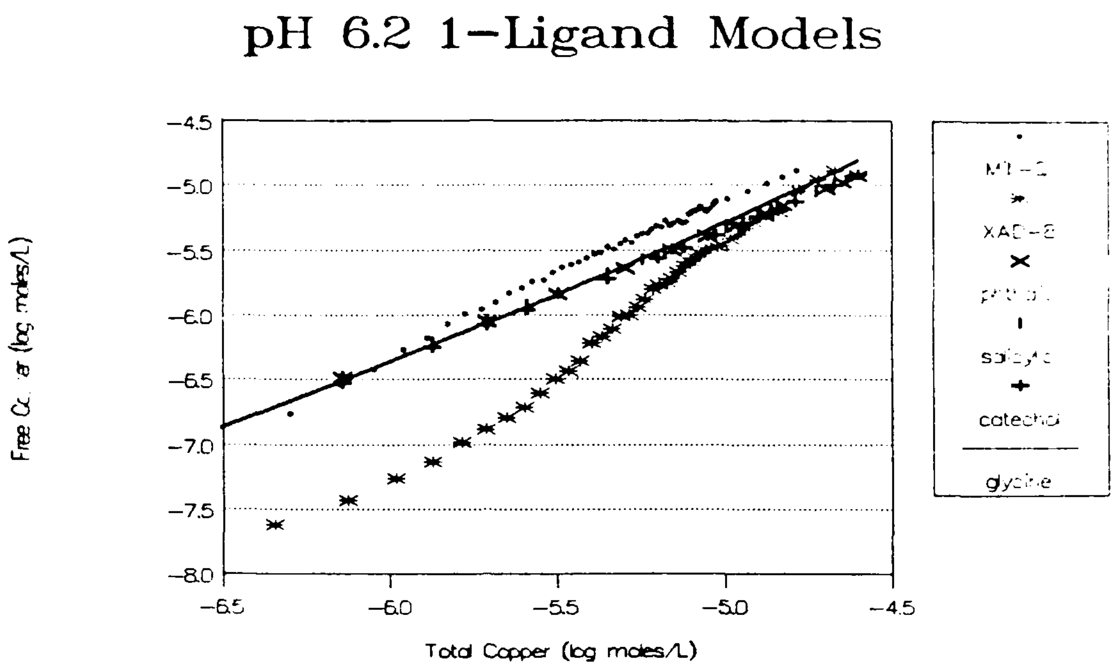


Figure 4.11 OCGW XAD-8 single model compound SAS fitting (see Table 4.4)



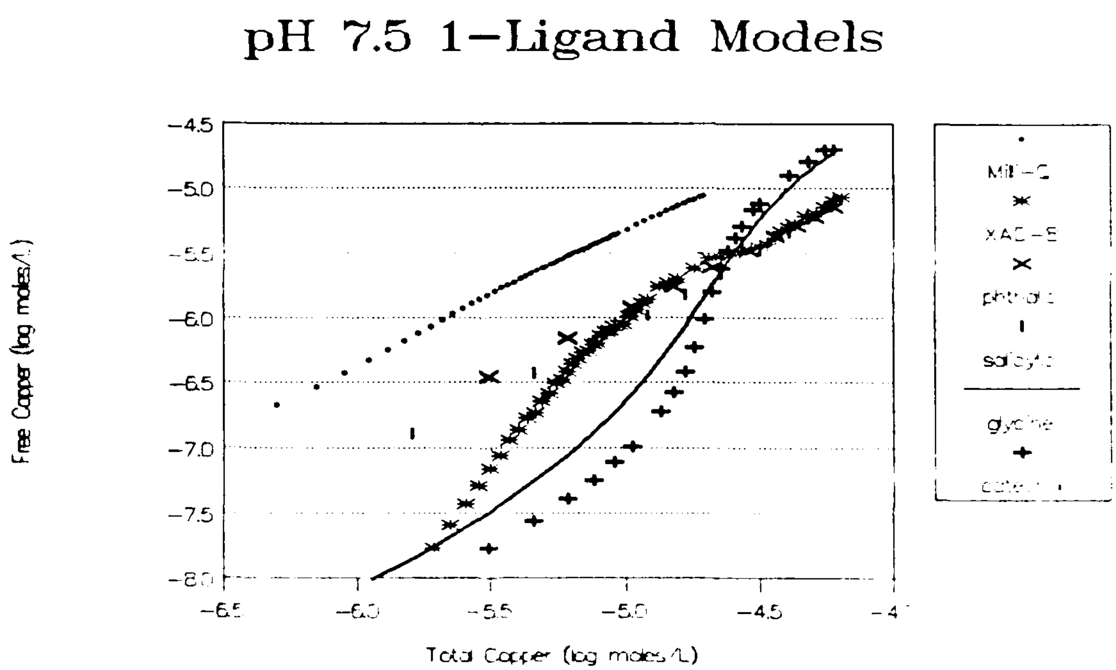


Figure 4.12 BA XAD-8 single model compound SAS fitting (see Table 4.4)

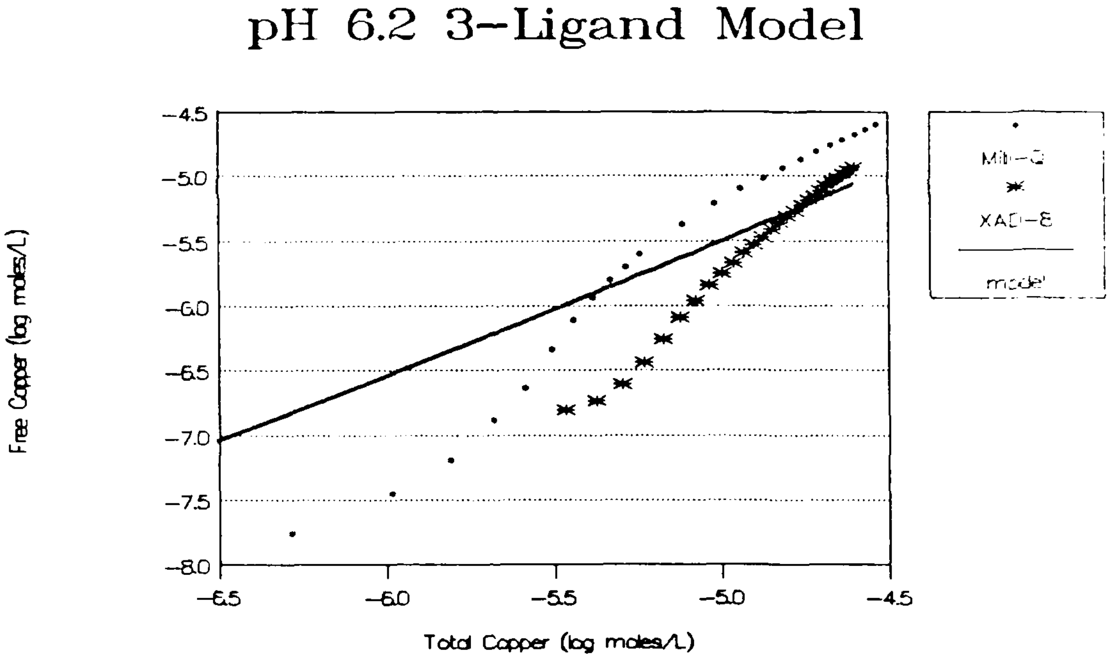
Table 4.4 SAS modeling concentrations

	CONCENTRATIONS (pL)			
	OCGW (DOC=5.66 mg/L)		BA (DOC=5.02 mg/L)	
	pH 6.2	pH 7.5	pH 6.2	pH 7.5
1-ligand Fit				
catechol	4.2	4.2	4.3	4.7
glycine	4.5	4.1	4.8	4.55
phthalic acid	3.83	2.703	3.9	3.13
salicylic acid	3.6	3.595	3.7	4.0
2-ligand Fit				
catechol	4.2	4.6	4.2	5.03
phthalic acid	4.25	2.86	4.6	3.25
3-ligand Fit				
catechol	4.434	5.3	4.91	5.3
phthalic acid	4.4	2.78	8.02	3.3
glycine	5.0	5.0	5.1	5.1

Table 4.5 Composition of SAS modeling three ligand fits

Elemental Percentages	OCGW (DOC=5.66 mg/L) pH 6.2	OCGW (DOC=5.66 mg/L) pH 7.5	BA (DOC=5.02 mg/L) pH 6.2	BA (DOC=5.02 mg/L) pH 7.5
C	66.5 +	43.6	60.6	57.7
H	5.0	27.3 +	5.7	3.7
O	27.1 +	29.0 -	31.0	38.5
N	1.2	0.04 --	2.7	0.1 --
Total	99.8	99.94	100	100
Ratios				
H/C	0.90	7.48 ++	1.11 +	0.76 -
O/C	0.31 -	0.50	0.38 -	0.50
N/C	0.02	0.0008 -	0.04	0.002 -
Acidity (meq/g-C)				
Carboxylic	16.03 -	586.4 ++	0.004 --	199.7++
Phenolic -OH	14.12 +	1.77 -	4.92	1.20 -

+ high
++ very high
- low
-- very low



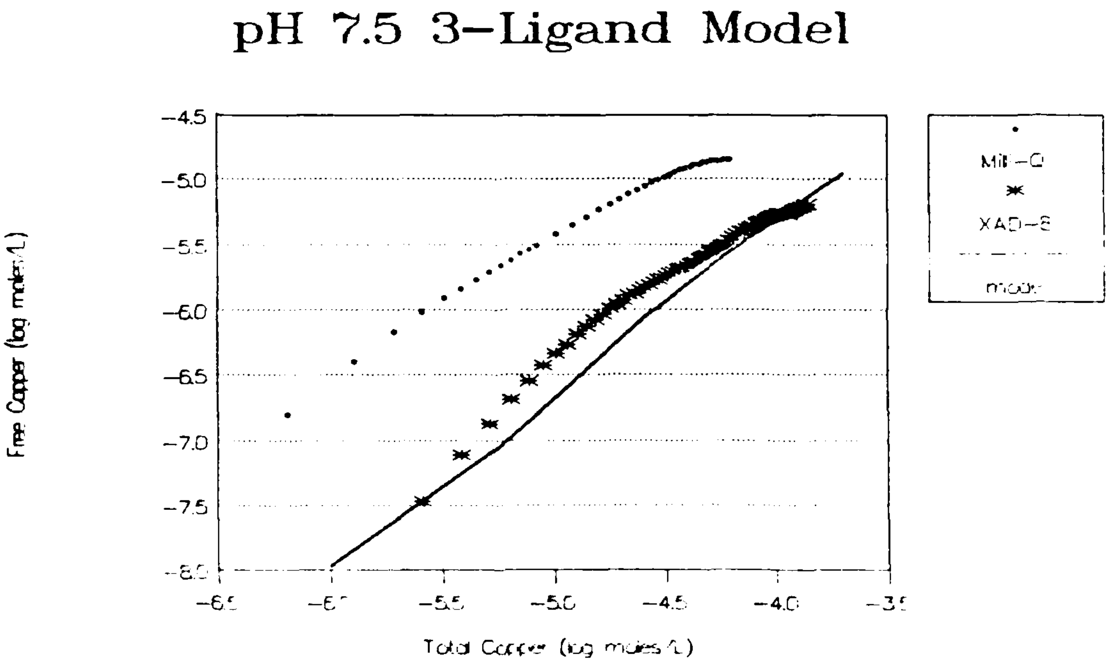
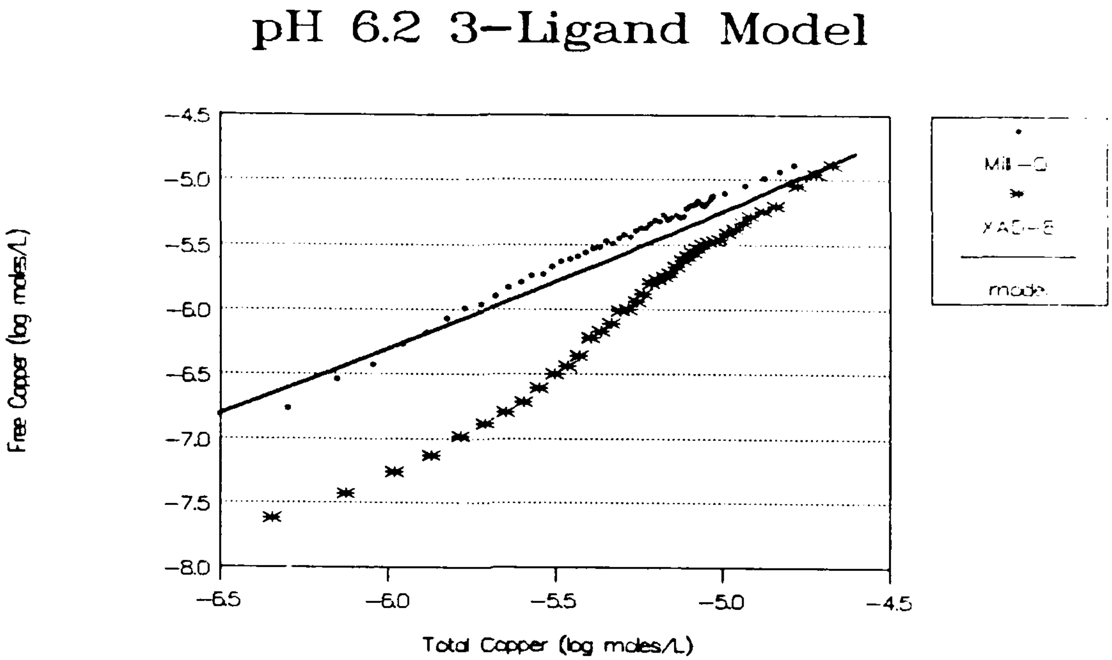


Figure 4.13a OCGW XAD-8 3-ligand SAS fitting
(pH 6.2 XAD-8 corrected for blank)



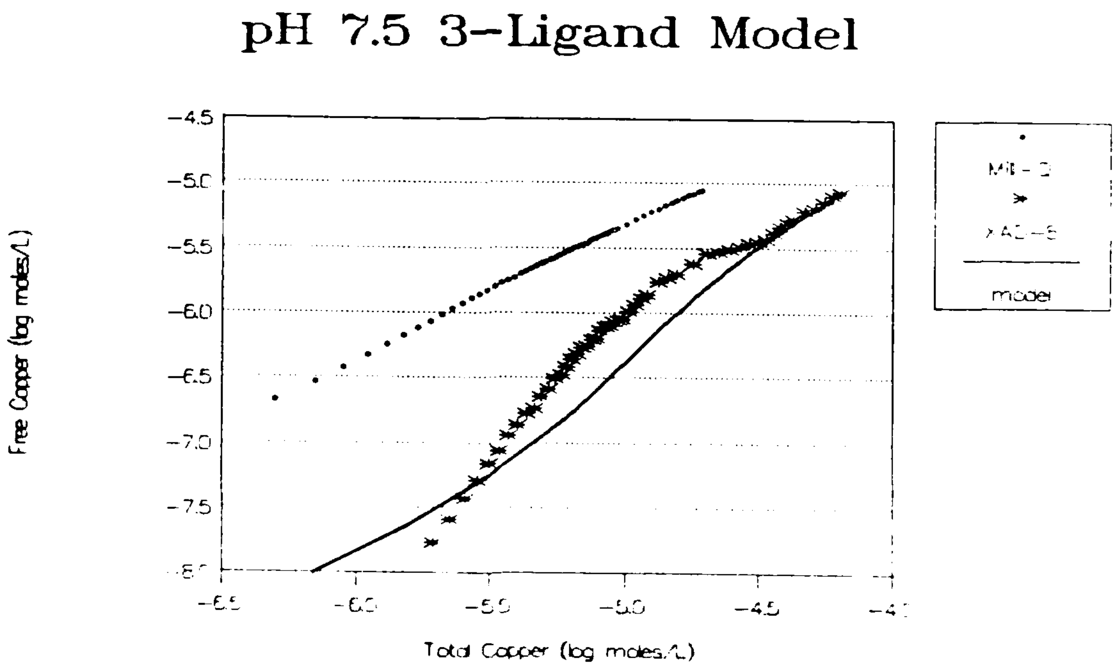


Figure 4.13b BA XAD-8 3-ligand SAS fitting

To show that modeling mixtures were as expected for the actual titrations, the OCGW model mixture for pH 6.2 was titrated (see Table 4.6). Figure 4.14 shows the results of the potentiometric and complexometric titrations with the outcome as expected. For the potentiometric curve, the titration is positioned to the left of the Milli-Q titration due to the basic condition caused by the presence of glycine.

Table 4.6 Composition of titrated mixture

		OCGW Model (DOC=5.66 mg/L)	Average HA (Lamy,et al., 1987; Steelink, 1985; Thurman, 1985)
Compound concentrations (pL)			
catechol		4.849	
phthalic acid		4.254	
glycine		5.00	
Elemental percentages			
	C	57.2	40-60
	H	4.1	4-6
	O	37.5	30-50
	N	1.2	1-6
Ratios			
	H/C	0.85	0.91
	O/C	0.49	0.50
	N/C	0.02	0.04
Acidity (meq/g-C)			
Carboxylic		19.7	
Phenolic		5.0	

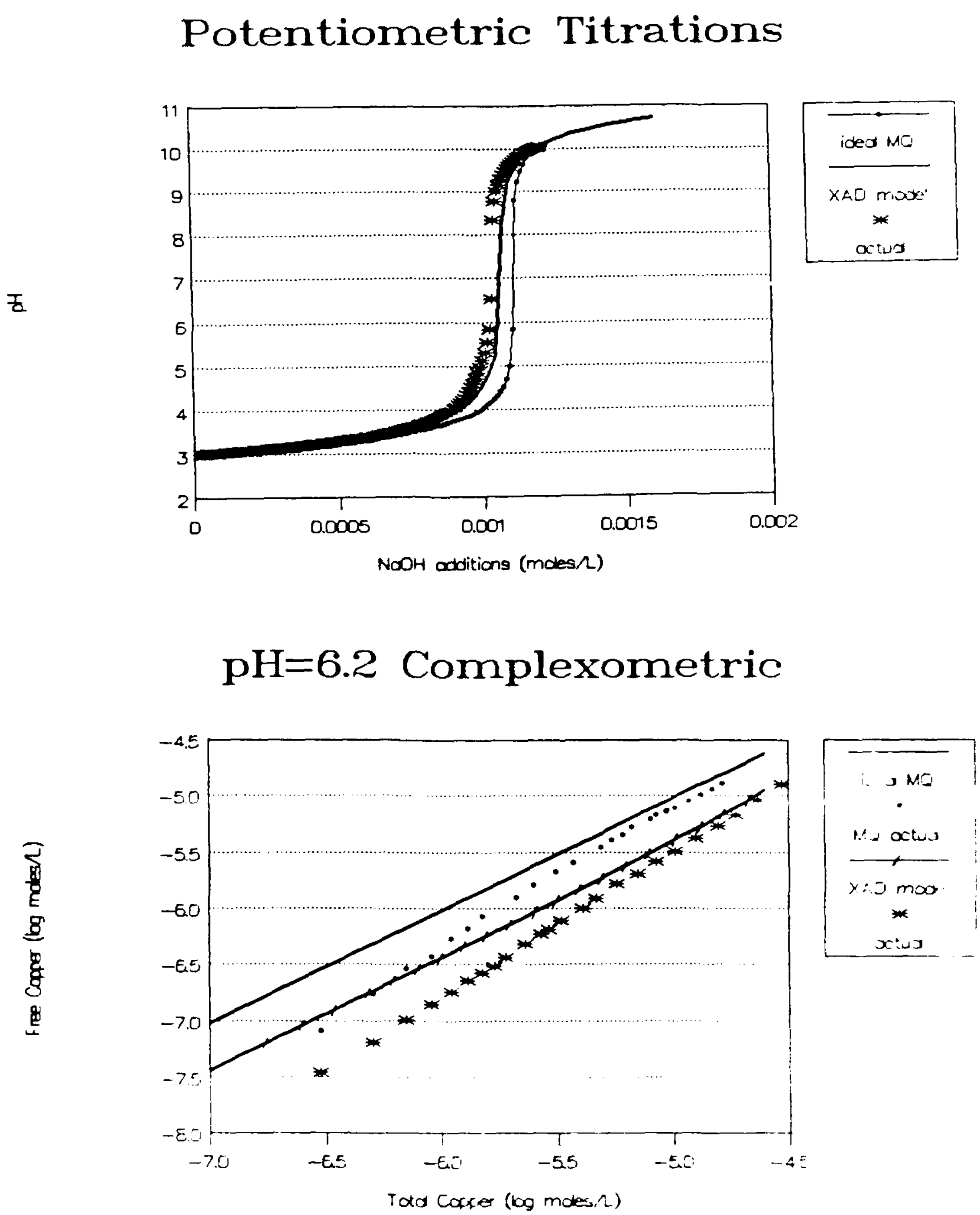


Figure 4.14 Titration of OCCW model mixture

4.4 **Other Modeling Attempts**

Without any further titrations, each of the natural sources were modeled with other amino acids because glycine did not provide enough binding capacity.

4.4.1 OCGW XAD-8 Modeling

Using the pH 6.2 complexometric data and concentrations of catechol and glycine, the SAS program was allowed to fit for a third ligand concentration and binding constant. The result was a pL of 5.20 and a binding constant of 9.00 for a non-protonated binding site. In Smith and Martell (1975), two possible compounds were found that fit the binding constant requirement: N-N-glycine and N-Uriodoiminodiacetic acid (N-U acid). Properties of these two amines are shown in Table 4.7.

Using assumptions (1) to (4), concentrations of phthalic acid and catechol were modeled with SAS for both amino acids at pH 6.2 and 7.5. The results are shown in Table 4.8 with calculated chemical compositions. Figure 4.15 shows the potentiometric and complexometric plots of the mixtures with better results than the previous ligand used, glycine.

For both pH models, the potentiometric plots fit close to one another but not near to the actual XAD-8 titration. In Figure 4.15 the pH 6.2 model mixture fit better on the upper portion of the complexometric curve but had too much binding at the lower portions of the curve. The pH 6.2

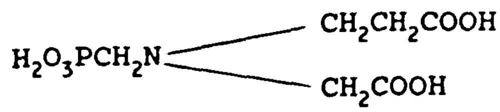
Table 4.7 Other amino acids (Smith and Martell, 1975)

Name:

N-(Phosphonomethyl)-N-(2-cargoxethyl) glycine or (N-(phosphonomethyl) glycine-N-propanoic acid (H_4L)

Chemical formula: $C_6H_{12}O_7NP$

Structure:



Constants (log K):

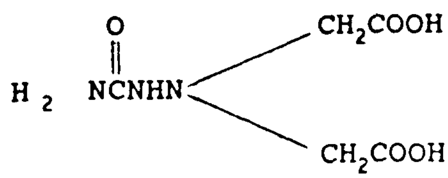
HL/H.L	10.41
H_2 L/HL.H	5.59
H_3 L/H_2L.H	3.48
H_4 L/H_3L.H	2.72
CuL/Cu.L	13.0
CuHL/CuL.H	4.71

Name:

N-Uriodoiminodiacetic acid (H_2L)

Chemical Formula: $C_5H_9O_5N_3$

Structure:



Constants (log K)

HL/H.L	4.04
H_2 L/HL.H	2.96
CuL/Cu.L	8.40

Table 4.8 Amino acid modeling elemental compositions and ratios - OCGW XAD-8

	OCGW XAD-8			
	pH 6.2 with		pH 7.5 with	
	N-N-gly	N-U acid	N-N-gly	N-U acid
Mixture (pL - %)-the same for both amino acids				
amine	5.2 - 8.9 %		4.35	
catechol	4.85 - 20.0 %		4.85	
phthalic	4.3 - 71.0 %		4.96	
Percentages				
C	55.1	45.4	37.4 -	39.9
H	4.1	4.3	4.9	4.7
O	38.3	39.4	43.5	39.7
N	0.8 -	10.8 +	4.4	15.7 +
P	1.7 +	---	9.8 ++	---
Ratios				
H/C	0.88	1.14 +	1.56 +	1.39 +
O/C	0.52	0.65 +	0.87 +	0.75 +
N/C	0.01 -	0.20 +	0.10 +	0.34 +

\+ high
++ very high
\- low
-- very low

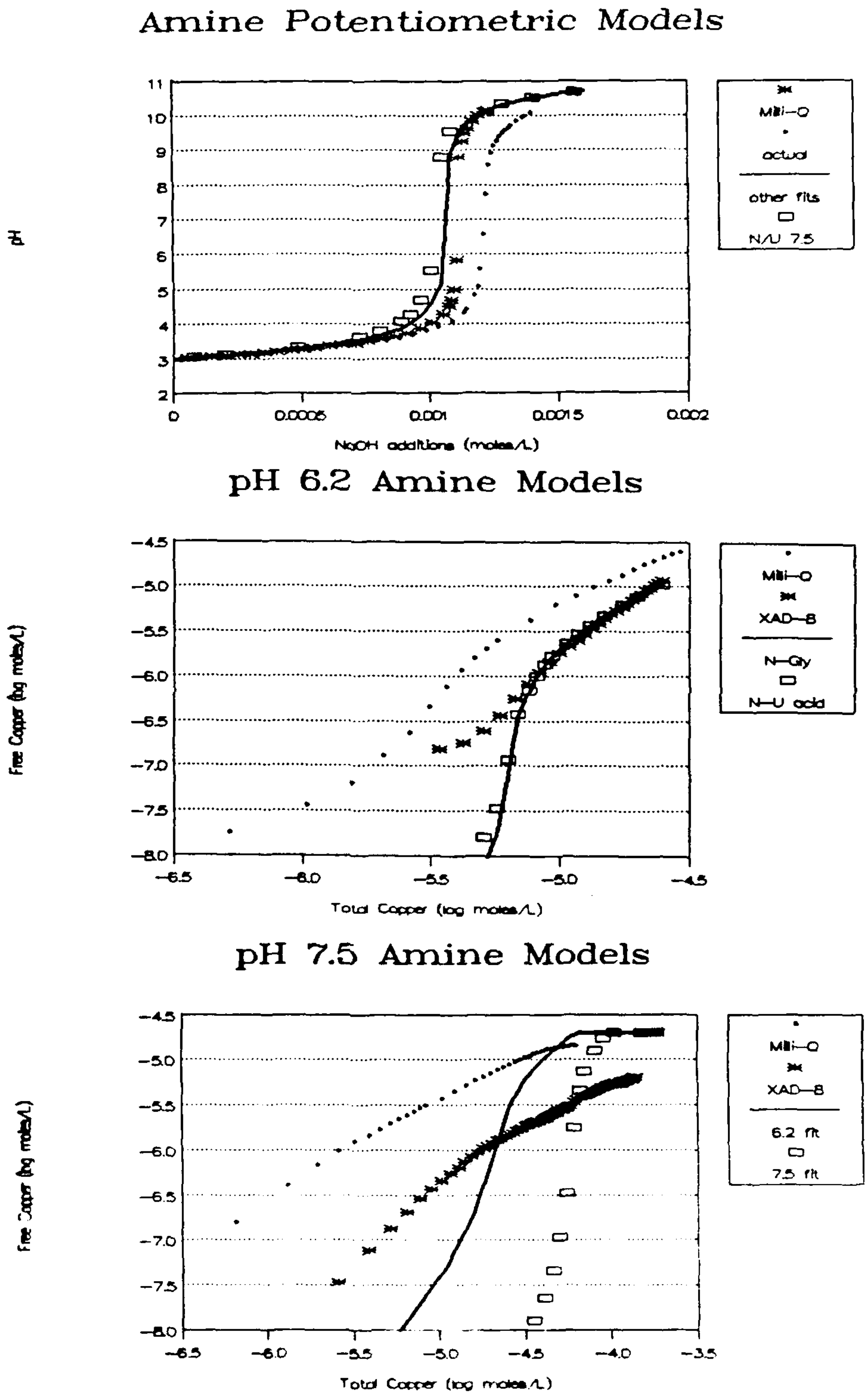


Figure 4.15 OCGW XAD-8 amine titration models (with pH 6.2 model mixture shown on the pH 7.5 graph)

modeling concentrations were compared to the 7.5 concentrations and showed no match nor a fit to the actual titration.

4.4.2 BA XAD-8 Modeling

Concentrations for the two amines were determined similarly to OCGW modeling (see Table 4.9). Also similar to OCGW modeling, only the pH 6.2 titration showed a good fit with the stronger amine models (see Figure 4.16) but with too much binding occurring at the lower portions of the curves.

4.4.3 Fitting pH 7.5 Titrations

The fitting of each of the pH 7.5 titrations came about by using the concentrations of catechol and phthalic acid obtained from the 3-ligand fitting with SAS (see Table 4.5) and substituting the stronger binding amines of N-N-glycine and N-U acid for glycine. The pL concentration of each amine required to fit the data was 5.4 for both water sources. The results of the fitting are shown in Figure 4.17. Acidities for the model mixtures to fit the pH 7.5 titrations were even higher than that shown in Table 4.5.

Table 4.9 Amino acid modeling elemental compositions and ratios - BA XAD-8

	BA XAD-8			
	pH 6.2 with		pH 7.5 with	
	N-N-gly	N-U acid	N-N-gly	N-U acid
Mixture (pL - %)-the same for both amino acids				
amine	5.4 - 12.0 %		5	
catechol	5.2 - 19.0 %		5.2	
phthalic	4.64 - 69.0 %		4.77	
Percentages				
C	53.9	55.0	47.3	49.5
H	4.1	4.0	4.5	4.3
O	38.7	37.8	40.6	38.4
N	1.0	3.28	2.4	7.8 +
P	2.3 ++	---	5.2 ++	---
Ratios				
H/C	0.91	0.88	1.11 +	1.03 +
O/C	0.54	0.52	0.64 +	0.58 +
N/C	0.02	0.05	0.04	0.01 -

+ high
++ very high
- low
-- very low

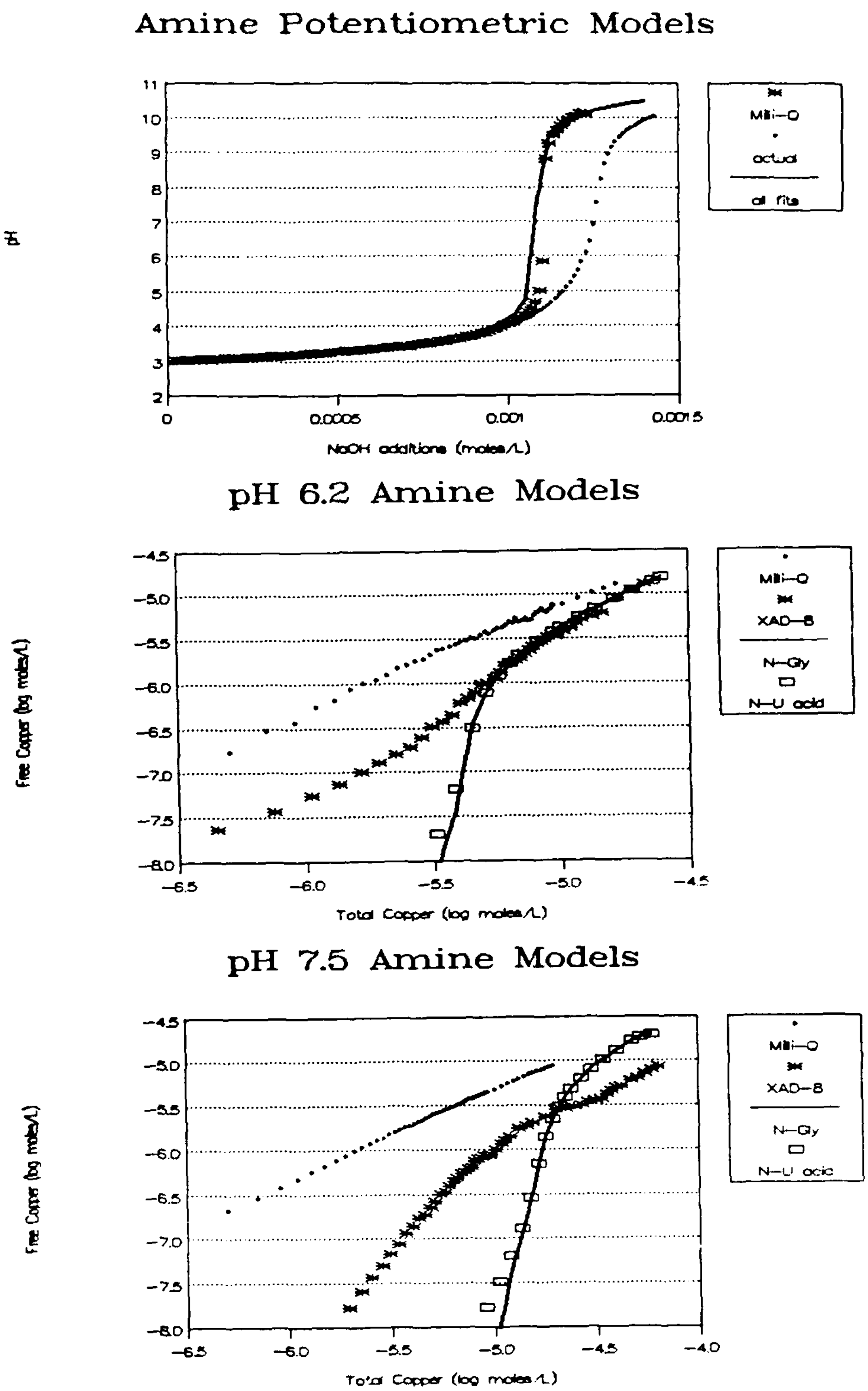
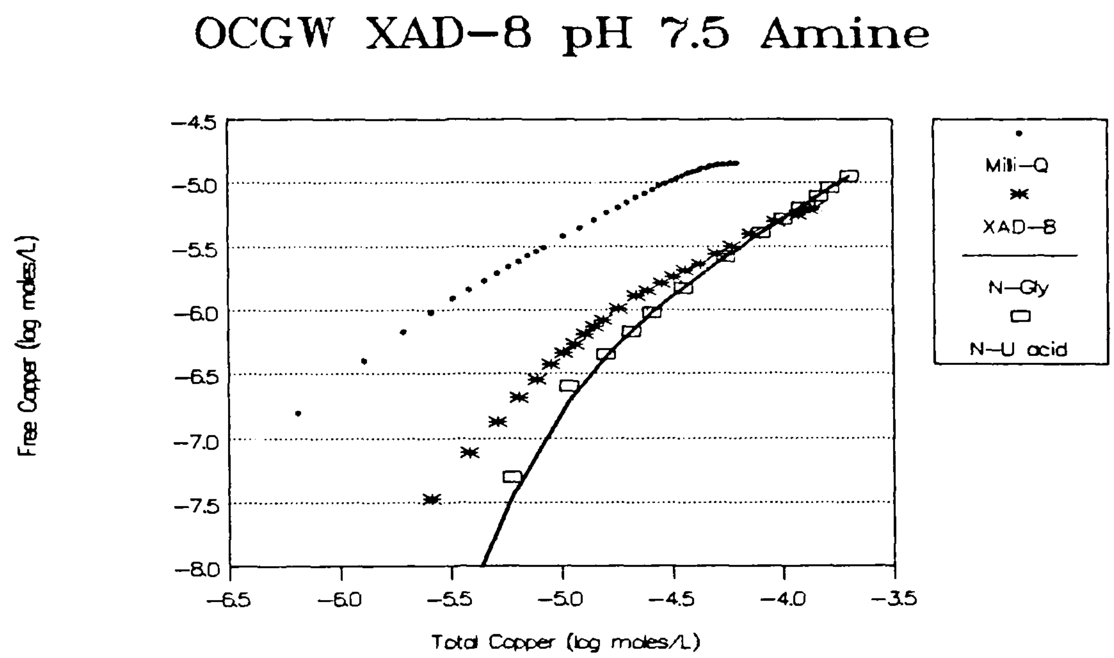


Figure 4.16 BA XAD-8 amine titration models



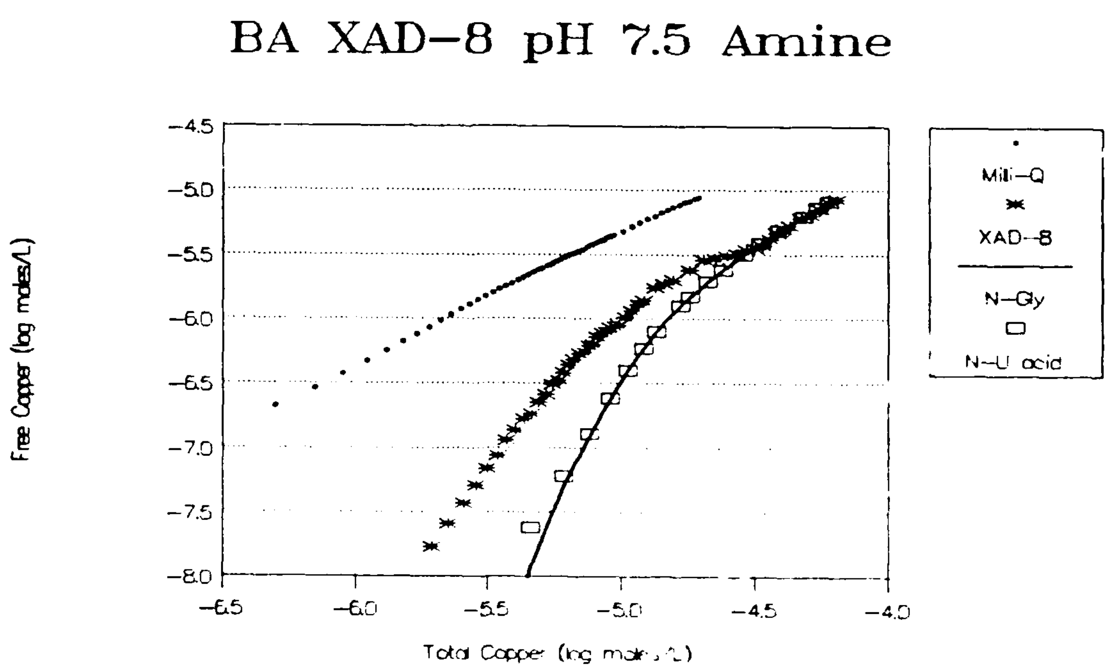


Figure 4.17 pH 7.5 fitting

CHAPTER 5

DISCUSSION

Although the results of the experimentation and modeling did not achieve the objective of developing a model of a humic substance based on a combination of ligands, it does give further insight into the behavior of a humic substance in an experiment protocol.

5.1 **Titration Experiments**

5.1.1 Model Compound Binding Constants

Verifying published binding constants for each of the model compounds to those experimentally obtained was necessary because of the dependence on temperature and ionic strength. Although experimental temperatures and ionic strengths did change the binding by no more than 1/2 an order of magnitude, modeled curves fitted well with experimental curves. Temperature and ionic strength corrections were inherent in TITRATOR and were, therefore, not required for modeling. Salicylic acid was the only compound which did not agree with the published binding constants. In this case, experimental values were used since the published values did not fit either complexometric titration at pH 6.2 or 7.5.

Compared to Ephraim's, et al. (1989), work identifying 30 - 45 percent of acidic sites responsible for copper

binding to a salicylic acid-like group and 25 - 30 percent as a catechol-like group for an aquatic fulvic acid, this research found for the models that fit the complexometric curves at pH 6.2, 70 percent of the copper binding was by phthalic acid groups, 20 percent for catechol, and 10 percent by amines for an aquatic humic acid. Work at pH 7.5 showed less than 1 - 2 percent of the groups responsible for copper binding were of the catechol and amine type, and a large percentage (> 98 percent) characterized a phthalic acid-type group.

5.1.2 Titration Vessel Interferences

As shown in Figure 3.4, the type of titration vessel used will effect complexometric results. The decrease of free copper with glass was observed by Cabaniss and Shuman (1988c) along with no decrease observed in opaque, teflon beakers. This study showed slight interferences with polypropylene which may have not been due to adsorption. In comparing glass and polypropylene titrations, though, glass had much higher adsorption of copper (II) occurring.

5.1.3 Titration Reliability

Repeats done on glycine showed good repeatability for potentiometric titrations. Error bars for complexometric titrations did not, however, show as good a repeatability. At the lower portions of the titration curve, where free copper was less than 10^{-7} M, some error was expected due to the loss of linearity with the copper probes. The error for

the titration was at its lowest at a total copper concentration of $10^{-5.5}$ M, and increased from that point with increasing total copper concentration. This trend can be explained by the number of binding sites for the ligands being occupied decreasing as more copper is introduced. The remaining ligand sites take a longer time to be occupied by the free copper; therefore, enough time should pass before further copper additions. In this research, titrations were automated, and ten minutes were allowed between copper additions. Cabaniss and Shuman (1988a) allowed 3 to 30 minutes between additions, depending on the total copper concentration. Holm and Curtiss (1990) equilibrated for 60 minutes.

Between the two pH titrations, the pH 7.5 titrations had greater error than the pH 6.2 titrations. This could be due to the presence of another ligand (OH^-) requiring even longer equilibration times. It may have been also due to the difficulty experienced in maintaining a constant pH at 7.5. A HEPES concentration of 5 mM was found to be adequate to maintain the pH to $\pm$ .01 units. Holm and Curtiss (1990) buffered their titrations with HEPES at 6.7 mM.

5.2 Model Compound Mixtures

The selection of the model compounds used - catechol, phthalic acid and salicylic acid - was partially based on previous work that attributed binding sites of humic substances to these groups on humic substance molecules (see Section 2.2). Of the previous work, this research effort agreed with Buffle, et al. (1980), in showing that salicylic and phthalic acids do not have high enough binding capacities to explain a humic substance. Also in this research, catechol and glycine were not adequate. What was also shown is that if it is assumed that phenolic and carboxyl groups are responsible for the majority of the complexation of metals that occurs, then phenolic acidity measurements limit the use of salicylic acid and catechol quantities. With the similarity in behaviors of salicylic acid and phthalic acid in modeling each of the groundwater sources, chemical constraints of phenolic -OH content required the use of phthalic acid and catechol to describe the complexation of copper (II) by a humic substance. In previous work that had carboxylic acidities closer to phenolic acidities, salicylic acid-type groups may have been more appropriate.

5.2.1 OCGW XAD-8 Mixtures

For this groundwater source, phthalic acid and catechol did not adequately model the complexometric curves. The addition of glycine was also not successful. The

substitution of glycine with N-N-glycine and N-U acid did fit the titration at pH 6.2, but there too much binding occurring at the lower portions of the curve. This indicated that the nitrogen content used was excessive. Problems occurred when concentrations of phthalic acid, catechol and the higher binding amino acids were modeled to the pH 7.5 titrations. The parameters which provided a good fit at pH 6.2 titrations were not adequate to explain pH 7.5 titrations. Only by using the high phthalic acid concentrations from the 3-ligand fitting was a good fit approached with the higher binding amino acids. The result though of using the higher concentration of phthalic acid was a mixture that did not contain a reasonable carboxylic acidity. Use of the higher binding amino acids also caused a poor fit of the potentiometric curves due to the loss in overall acidity.

5.2.2 BA XAD-8 Mixtures

Modeling of the BA XAD-8 groundwater had the same results as OCGW. Final fitting of the pH 6.2 complexometric titration was possible with catechol, phthalic acid and N-N-glycine or N-U acid; but this combination of ligands gave a poor fit to potentiometric data. The same concentrations did not fit the pH 7.5 titrations, and fitting was possible by using high concentrations of phthalic acid. The phthalic acid concentration was not as high for BA as OCGW due to the lower carboxylic content of BA.

5.2.3 Possible Other Functional Groups

The results indicated that the complexation behavior of a humic acid is best modeled by a strong amino acid at pH 6.2 and with carboxylic and phenolic groups. Titrations at pH 7.5 needed a strong carboxylic-type group for proper fitting. For a model mixture to fit at both pHs, the carboxylic-type group would need to have a strong unprotonated binding ligand at pH 7.5 that dominates the speciation. At pH 6.2, a relatively-weak, protonated ligand would need to dominate. This suggests a site with an acid dissociation constant between 6.2 and 7.5 and a multidentate character.

Even if such a ligand was available, the necessity of also fitting potentiometric curves and satisfying reasonable concentrations and elemental percentages and ratios may not be possible. For example, the carboxylic acidities may be exceeded by such a ligand to fit the pH 7.5 titrations. An increased binding with pH might be due to another minor functional group such as the sulfur groups. However, at this point the model system begins to mirror the complexity of the item being modeled.

CHAPTER 6

CONCLUSIONS

6.1 Chemical Modeling of a Humic Acid

This research project set out to find a simple model mixture for a highly complex system. The model had to fit the constraints of being chemically-valid and of being able to describe experimental data. In attempting to characterize a groundwater humic/fulvic acid with simple model compounds, some of the constraints were satisfied for some of the conditions. The modeling of a humic substance was possible at pH 6.2 with phthalic acid, catechol and N-N-glycine, but the presence of N-N-glycine reduced the mixture acidity and caused an improper characterization of potentiometric data. At pH 7.5, experimental fitting of the complexometric curves was possible with the same compounds, but with high concentrations of phthalic acid, resulting in carboxylic acidities that were excessive. Carboxylic and phenolic acidities occurring as multidentate ligands would better model the complexation behavior of humic substances than the excessive binding observed by nitrogen present as amino acids. The low concentrations of highly complexing nitrogen did not characterize the behavior of the humic substances properly.

6.2 Recommendations for Future Work

Future work of finding a simple model for a humic substance should begin with a systematic approach of modeling a proposed model mixture with the computer programs available prior to expending time in the laboratory. Experimental verification is the final and necessary step to the modeling process of the model compound constants and the model mixtures. The apparatus for complexometric titrations should include the use of appropriate, non-adsorbing titration vessels. Polypropylene or opaque teflon should be adequate. Temperature control of complexometric titrations is not as vital as for potentiometric titrations, but for consistency, a jacketed, temperature-controlled, vessel would be ideal. The DOC of the titrated natural sources should be kept between 4 - 6 mg/L to ensure adequate response for the titration range of copper (II). The titrant additions are also important and should be between 2 X 10^{-5} M and 2 X 10^{-4} M per addition of copper (II). One item not fully recognized in this research was the long equilibration times required as total copper concentration increases. Automated programs can be adjusted so that longer times are allowed as the titration progresses. An increase in time will likely result in the need for greater buffering capacity. The effects of increasing buffering should be examined as buffer concentrations begin to overwhelm the ligand concentrations.

APPENDICES

Appendix A Titration Data of Single Model Compounds

Model Compound Potentiometric Titrations

(Phth,Cat,Sal-by Len Rothfield) (Glys-Castro)

Phthalic Acid [NaOH]	pH	Catechol [NaOH]	pH	Salicylic Acid [NaOH]	pH
0	2.95	0	6.5	0	2.9
0.000107	3.07	5.33E-05	7.6	5.33E-06	2.93
0.000213	3.11	0.000107	8	1.07E-05	2.95
0.000266	3.14	0.00016	8.5	1.6E-05	2.97
0.000319	3.21	0.000213	8.6	4.26E-05	3
0.000372	3.29	0.000266	8.74	5.86E-05	3.02
0.000424	3.36	0.000398	9	7.99E-05	3.04
0.00053	3.5	0.00053	9.1	0.000107	3.06
0.000582	3.64	0.000661	9.25	0.000133	3.08
0.000645	3.71	0.000792	9.4	0.00016	3.09
0.00074	3.86	0.000923	9.6	0.000213	3.13
0.000792	4.1	0.001053	9.75	0.000266	3.16
0.000897	4.4	0.001182	9.85	0.000319	3.2
0.000949	4.5	0.001311	10	0.000372	3.24
0.001053	4.75	0.00144	10.2	0.000451	3.29
0.001105	4.8	0.001569	10.35	0.000535	3.36
0.001156	5	0.001697	10.48	0.000635	3.45
0.00126	5.2	0.001824	10.55	0.000687	3.52
0.001311	5.3	0.001951	10.65	0.00074	3.59
0.001363	5.4	0.002078	10.75	0.000844	3.75
0.00144	5.5	0.002204	10.8	0.000895	3.88
0.001517	5.85	0.00233	10.85	0.000949	4.16
0.001569	6	0.002456	10.9	0.000975	4.39
0.001579	6.1	0.002581	10.95	0.001001	4.78
0.001594	6.25			0.001027	6.17
0.00162	6.65			0.001032	8.76
0.001633	7.25			0.001037	9.1
0.001645	8			0.001042	9.32
0.001656	8.8			0.001047	9.44
0.001658	9.3			0.001053	9.69
0.001671	9.6			0.001068	9.8
0.001697	9.7			0.001084	9.85
0.001722	9.8			0.001094	9.9
0.001748	9.87			0.001105	9.94
0.001773	9.9			0.001115	9.99
0.001824	10.1			0.00112	10.01
				0.001125	10.03
				0.00113	10.06

Glycine [NaOH]	pH	Glycine Repeat [NaOH]	pH
1.06E-05	3.001	1.07E-05	3
2.13E-05	3.006	2.13E-05	3.005
4.26E-05	3.015	3.2E-05	3.01
6.38E-05	3.025	4.26E-05	3.014
8.51E-05	3.036	5.33E-05	3.019
0.000106	3.046	6.39E-05	3.024
0.000128	3.058	7.45E-05	3.029
0.000149	3.069	8.52E-05	3.033
0.00017	3.081	9.58E-05	3.039
0.000191	3.092	0.000106	3.044
0.000212	3.105	0.000117	3.05
0.000234	3.118	0.000128	3.055
0.000255	3.131	0.000138	3.06
0.000276	3.145	0.000149	3.065
0.000297	3.16	0.00016	3.071
0.000318	3.174	0.00017	3.076
0.000339	3.19	0.000181	3.083
0.000381	3.225	0.000191	3.089
0.000403	3.242	0.000202	3.094
0.000424	3.26	0.000213	3.101
0.000445	3.282	0.000223	3.106
0.000466	3.303	0.000234	3.113
0.000487	3.324	0.000244	3.119
0.000508	3.348	0.000255	3.126
0.000529	3.372	0.000266	3.133
0.00055	3.399	0.000276	3.14
0.000571	3.427	0.000287	3.146
0.000592	3.459	0.000297	3.152
0.000613	3.491	0.000308	3.159
0.000634	3.528	0.000318	3.166
0.000655	3.569	0.000329	3.174
0.000676	3.613	0.00034	3.182
0.000697	3.664	0.00035	3.189
0.000718	3.722	0.000361	3.196
0.000738	3.787	0.000371	3.205
0.000759	3.867	0.000382	3.212
0.00078	3.962	0.000392	3.221
0.000801	4.088	0.000403	3.229
0.000822	4.264	0.000414	3.238
0.000843	4.547	0.000424	3.247
0.000864	5.183	0.000435	3.255
0.000885	7.01	0.000445	3.264
0.000905	7.497	0.000456	3.275
0.000926	7.731	0.000466	3.283
0.000947	7.891	0.000477	3.294
0.000968	8.006	0.000487	3.304
0.000988	8.105	0.000498	3.315
0.001009	8.186	0.000508	3.325
0.00103	8.258001	0.000519	3.337
0.001051	8.321	0.000529	3.348
0.001071	8.376001	0.00054	3.36
0.001092	8.428001	0.00055	3.372
0.001113	8.474	0.000561	3.385
0.001134	8.517	0.000571	3.398
0.001154	8.559	0.000582	3.412
0.001175	8.596	0.000592	3.426
0.001196	8.632	0.000603	3.44

Glycine

[NaOH]	pH
0.001237	8.698
0.001258	8.729999
0.001278	8.759
0.001299	8.788999
0.001319	8.814999
0.00134	8.840999
0.001361	8.866999
0.001381	8.892
0.001402	8.917
0.001422	8.939999
0.001443	8.962
0.001463	8.984999
0.001484	9.007
0.001504	9.028
0.001525	9.049
0.001545	9.068
0.001566	9.089
0.001586	9.109
0.001607	9.128
0.001627	9.148
0.001648	9.165
0.001668	9.185001
0.001688	9.203
0.001709	9.222
0.001729	9.239001
0.00175	9.257
0.00177	9.274999
0.00179	9.292
0.001811	9.311
0.001831	9.326
0.001851	9.343001
0.001872	9.359999
0.001892	9.377
0.001912	9.392999
0.001933	9.409001
0.001953	9.425999
0.001973	9.441
0.001993	9.458
0.002014	9.474
0.002034	9.49
0.002054	9.505
0.002074	9.522001
0.002094	9.537
0.002115	9.552
0.002135	9.569
0.002155	9.583999
0.002175	9.599
0.002195	9.614001
0.002215	9.632
0.002236	9.646
0.002256	9.662
0.002276	9.678001

Glycine Repeat

[NaOH]	pH
0.000624	3.47
0.000634	3.486
0.000645	3.503
0.000655	3.521
0.000666	3.54
0.000676	3.559
0.000687	3.58
0.000697	3.6
0.000708	3.623
0.000718	3.647
0.000729	3.672
0.000739	3.7
0.00075	3.728
0.00076	3.759
0.000771	3.792
0.000781	3.83
0.000791	3.87
0.000802	3.914
0.000812	3.964
0.000823	4.018
0.000833	4.083
0.000844	4.159
0.000854	4.249
0.000864	4.363
0.000875	4.509
0.000885	4.705
0.000896	5.009
0.000906	5.624
0.000917	6.801
0.000927	7.229
0.000937	7.451
0.000948	7.605
0.000958	7.723
0.000969	7.816
0.000979	7.89
0.000989	7.956
0.001	8.029
0.001021	8.113
0.001041	8.199001
0.001062	8.273
0.001083	8.337
0.001104	8.395001
0.001124	8.446999
0.001145	8.496
0.001166	8.54
0.001186	8.58
0.001207	8.619001
0.001228	8.655
0.001248	8.689
0.001269	8.722
0.00129	8.754
0.00131	8.783

Glycine

[NaOH]	pH
0.002296	9.693
0.002316	9.708
0.002336	9.724
0.002356	9.741
0.002376	9.755999
0.002396	9.771
0.002416	9.786
0.002436	9.802
0.002456	9.818
0.002476	9.833999
0.002496	9.850001
0.002516	9.865
0.002536	9.88
0.002556	9.896
0.002576	9.912
0.002596	9.927
0.002616	9.944
0.002636	9.958999
0.002656	9.974
0.002676	9.99
0.002696	10.004

Glycine Repeat

[NaOH]	pH
0.001331	8.812
0.001352	8.839
0.001372	8.866
0.001393	8.891
0.001413	8.916001
0.001434	8.941
0.001454	8.963
0.001475	8.986
0.001496	9.008001
0.001516	9.03
0.001537	9.050999
0.001557	9.071999
0.001578	9.092
0.001598	9.113
0.001619	9.130999
0.001639	9.151
0.001659	9.17
0.00168	9.189
0.0017	9.208
0.001721	9.225001
0.001741	9.244001
0.001762	9.260999
0.001782	9.279
0.001802	9.295999
0.001823	9.313
0.001843	9.332
0.001863	9.347999
0.001884	9.365
0.001904	9.380999
0.001924	9.397001
0.001945	9.413999
0.001965	9.43
0.001985	9.446
0.002005	9.461001
0.002026	9.475001
0.002046	9.487001
0.002086	9.517999
0.002127	9.549
0.002167	9.581001
0.002207	9.613

Glycine Repeat

[NaOH]	pH
0.002248	9.644
0.002288	9.675
0.002328	9.707
0.002368	9.739001
0.002409	9.771
0.002449	9.802
0.002489	9.833
0.002529	9.864001
0.002569	9.896
0.002608	9.928001
0.002648	9.958999
0.002688	9.991
0.002728	10.022
0.002768	10.053

Milli-Q Complexometric Titrations @ pH = 6.2

Milli-Q Blank @ pH 6.2 Polypropylene log [CuT]	log [CuF]	Milli-Q Blank @ pH 6.2 Glass (Waterbury,1990) log [CuT]	log [CuF]	Ideal Milli-Q @ pH 6.2 log [Cu]	Blank
-7.000	-7.532	-6.28483	-7.75338	-7	-7.01963
-6.523	-7.089	-5.9838	-7.44776	-6.03152	-6.05117
-6.301	-6.767	-5.80771	-7.18834	-5.75449	-5.77416
-6.155	-6.535	-5.68277	-6.88628	-5.5867	-5.60639
-6.046	-6.431	-5.58586	-6.64108	-5.46597	-5.48568
-5.959	-6.272	-5.50668	-6.34257	-5.37161	-5.39133
-5.886	-6.182	-5.43973	-6.11514	-5.29414	-5.31388
-5.824	-6.072	-5.38174	-5.94101	-5.22841	-5.24817
-5.770	-5.995	-5.33059	-5.80597	-5.17134	-5.19112
-5.722	-5.957	-5.28483	-5.69936	-5.1209	-5.1407
-5.678	-5.902	-5.24344	-5.60341	-5.07572	-5.09554
-5.639	-5.833	-5.11604	-5.37242	-5.0348	-5.05463
-5.603	-5.788	-5.01766	-5.21251	-4.9974	-5.01726
-5.570	-5.746	-4.9375	-5.10234	-4.96297	-4.98284
-5.539	-5.736	-4.86986	-5.0135	-4.93107	-4.95096
-5.510	-5.677	-4.81135	-4.93888	-4.90136	-4.92127
-5.481	-5.636	-4.75979	-4.87136	-4.87354	-4.89347
-5.457	-5.618	-4.71371	-4.8145	-4.84741	-4.86735
-5.433	-5.594	-4.67205	-4.76119	-4.82275	-4.84272
-5.410	-5.559	-4.63404	-4.71855	-4.79942	-4.81941
-5.389	-5.535	-4.59909	-4.67591	-4.77728	-4.79728
-5.368	-5.525	-4.56675	-4.63682	-4.75622	-4.77624
-5.349	-5.480	-4.53665	-4.60483	-4.73613	-4.75617
-5.330	-5.494	-4.50849	-4.57285	-4.71693	-4.73698
-5.312	-5.459	-4.48206	-4.54087	-4.69854	-4.71861
-5.294	-5.424	-4.45714	-4.51244	-4.68089	-4.70099
-5.278	-5.442	-4.43357	-4.48756	-4.66394	-4.68405
-5.262	-5.400	-4.41122	-4.46269	-4.64762	-4.66776
-5.246	-5.373	-4.38996	-4.44136	-4.6319	-4.65205
-5.231	-5.376	-4.3697	-4.41649	-4.61672	-4.63689
-5.217	-5.348	-4.35033	-4.39517	-4.60206	-4.62225
-5.203	-5.314	-4.3318	-4.3774		
-5.190	-5.331	-4.31402	-4.35608		
-5.177	-5.279	-4.29694	-4.33831		
-5.164	-5.314	-4.28051	-4.32054		
-5.152	-5.300	-4.26468	-4.30277		
-5.140	-5.279	-4.2494	-4.28856		
-5.128	-5.296	-4.23465	-4.27079		
-5.117	-5.283	-4.22037	-4.25302		
-5.106	-5.227	-4.20656	-4.24236		
-5.095	-5.206				
-5.084	-5.193				
-5.074	-5.172				
-5.064	-5.189				
-5.054	-5.203				
-5.04[illegible]	-5.182				
-5.03[illegible]	-5.161				
-5.0[illegible]1	-5.134				
-5.026	-5.127				
-4.9[illegible]1	-5.110				
-4.9[illegible]9	-5.047				
[illegible]	-4.[illegible]85				

log [CuT]	log [CuF]
-4.827	-4.943
-4.784	-4.888

COMPLEXOMETRIC TITRATIONS @ pH = 6.2 OF MODEL COMPOUNDS

Phthalic Acid (2.[illegible]8E-4M)
MES = .0001 M I=.01

log[CuT]	log[Cu]
-6.222	-7.024
-6.097	-6.862
-6.000	-6.741
-5.921	-6.640
-5.854	-6.559
-5.797	-6.485
-5.746	-6.423
-5.700	-6.369
-5.659	-6.319
-5.621	-6.268
-5.586	-6.229
-5.554	-6.191
-5.524	-6.152
-5.496	-6.121
-5.470	-6.086
-5.445	-6.055
-5.422	-6.032
-5.400	-6.000
-5.379	-5.977
-5.358	-5.959
-5.339	-5.931
-5.321	-5.904
-5.303	-5.884
-5.286	-5.865
-5.270	-5.845
-5.254	-5.826
-5.239	-5.807
-5.224	-5.791
-5.210	-5.776
-5.197	-5.756
-5.183	-5.744
-5.170	-5.725
-5.158	-5.710
-5.146	-5.698
-5.134	-5.682
-5.122	-5.65[illegible]
-5.111	-5.64[illegible]
-5.100	-5.628
-5.090	-5.628
-5.079	-5.616
-5.069	-5.605
-5.059	-5.593
-5.050	-5.582
-5.040	-5.570
-5.031	-5.558
-5.026	-5.547

Glycine (5E-5M) [MES] .0001M log[CuT]	log[CuI]	log[CuT]	log[CuI]	Gly (1e-4M) [MES]-.00[illegible]M log[CuT]	log[CuI]	log[CuT]	log[CuI]
-7.000	-7.653	-4.975	-5.649	-7.000	-7.867	-4.975	-5.963
-6.523	-7.374	-4.960	-5.624	-6.523	-7.639	-4.960	-5.917
-6.301	-7.224	-4.944	-5.599	-6.301	-7.465	-4.944	-5.867
-6.155	-7.066	-4.930	-5.578	-6.155	-7.337	-4.930	-5.817
-6.046	-6.959	-4.915	-5.553	-6.046	-7.227	-4.916	-5.778
-6.001	-6.916	-4.902	-5.531	-5.959	-7.139	-4.902	-5.807
-5.921	-6.830	-4.888	-5.511	-5.887	-7.060	-4.889	-5.764
-5.855	-6.758			-5.825	-6.997	-4.876	-5.729
-5.797	-6.694			-5.770	-6.936	-4.863	-5.689
-5.746	-6.637			-5.722	-6.886	-4.851	-5.654
-5.700	-6.583			-5.679	-6.837	-4.839	-5.618
-5.659	-6.537			-5.639	-6.791	-4.828	-5.586
-5.621	-6.494			-5.603	-6.751	-4.817	-5.554
-5.586	-6.451			-5.570	-6.712	-4.806	-5.523
-5.554	-6.415			-5.539	-6.677	-4.795	-5.494
-5.524	-6.379			-5.510	-6.641	-4.785	-5.462
-5.496	-6.343			-5.483	-6.606		
-5.470	-6.315			-5.458	-6.577		
-5.445	-6.283			-5.434	-6.542		
-5.422	-6.254			-5.411	-6.517		
-5.400	-6.225			-5.389	-6.485		
-5.379	-6.200			-5.369	-6.460		
-5.359	-6.175			-5.349	-6.435		
-5.339	-6.150			-5.330	-6.407		
-5.321	-6.125			-5.312	-6.386		
-5.303	-6.104			-5.295	-6.361		
-5.286	-6.079			-5.278	-6.336		
-5.270	-6.061			-5.262	-6.315		
-5.254	-6.039			-5.247	-6.297		
-5.239	-6.018			-5.232	-6.272		
-5.225	-6.000			-5.218	-6.254		
-5.210	-5.979			-5.204	-6.233		
-5.197	-5.961			-5.190	-6.215		
-5.183	-5.943			-5.177	-6.194		
-5.171	-5.925			-5.164	-6.176		
-5.158	-5.907			-5.152	-6.158		
-5.146	-5.893			-5.140	-6.141		
-5.134	-5.875			-5.128	-6.123		
-5.123	-5.857			-5.117	-6.105		
-5.111	-5.843			-5.106	-6.091		
-5.100	-5.828			-5.095	-6.073		
-5.090	-5.814			-5.085	-6.055		
-5.079	-5.800			-5.074	-6.041		
-5.069	-5.785			-5.064	-6.027		
-5.059	-5.771			-5.055	-6.013		
-5.050	-5.757			-5.045	-5.998		
-5.040	-5.746			-5.036	-5.981		
-5.026	-5.728			-5.027	-5.970		
-5.009	-5.699			-5.009	-6.073		
-4.992	-5.674			-4.992	-6.020		

Salicylic Acid (5.35766E-4M)
[MES]=.00052M I=.008

log[CuT]	log[CuF]
-6.999	-7.657
-6.522	-7.178
-6.301	-6.968
-6.155	-6.796
-6.045	-6.660
-5.958	-6.576
-5.886	-6.502
-5.824	-6.440
-5.770	-6.382
-5.721	-6.324
-5.678	-6.272
-5.639	-6.227
-5.602	-6.191
-5.569	-6.159
-5.538	-6.126
-5.509	-6.094
-5.482	-6.065
-5.457	-6.036
-5.433	-6.010
-5.410	-5.987
-5.388	-5.958
-5.368	-5.935
-5.348	-5.913
-5.329	-5.890
-5.311	-5.871
-5.294	-5.851
-5.277	-5.829
-5.261	-5.812
-5.246	-5.793
-5.231	-5.777
-5.217	-5.757
-5.203	-5.741
-5.189	-5.725
-5.176	-5.712
-5.163	-5.696
-5.151	-5.683
-5.139	-5.670
-5.128	-5.654
-5.116	-5.641
-5.105	-5.628
-5.094	-5.615
-5.084	-5.605
-5.074	-5.592
-5.064	-5.583
-5.054	-5.570
-5.044	-5.560
-5.035	-5.547
-5.026	-5.537
-4.991	-5.495
-4.959	-5.460
-4.929	-5.424
-4.901	-5.392
-4.875	-5.362
-4.850	-5.333
-4.827	-5.307
-4.805	-5.282

Catechol (1.36125E-M)
[MES]=.00048 I=.0008

log[CuT]	log[CuF]
-7.000	-7.545
-6.523	-7.205
-6.302	-7.011
-6.156	-6.862
-6.046	-6.751
-5.959	-6.662
-5.887	-6.585
-5.825	-6.522
-5.771	-6.461
-5.722	-6.407
-5.679	-6.363
-5.640	-6.322
-5.603	-6.283
-5.570	-6.249
-5.539	-6.217
-5.510	-6.182
-5.483	-6.153
-5.458	-6.125
-5.434	-6.099
-5.411	-6.071
-5.389	-6.048
-5.369	-6.026
-5.349	-6.001
-5.330	-5.982
-5.312	-5.963
-5.295	-5.940
-5.278	-5.921
-5.262	-5.905
-5.247	-5.886
-5.232	-5.867
-5.218	-5.851
-5.204	-5.836
-5.190	-5.820
-5.177	-5.804
-5.164	-5.791
-5.152	-5.775
-5.140	-5.762
-5.129	-5.747
-5.117	-5.734
-5.106	-5.721
-5.095	-5.708
-5.085	-5.696
-5.075	-5.683
-5.065	-5.670
-5.055	-5.658
-5.045	-5.648
-5.036	-5.639
-5.027	-5.626
-4.992	-5.616
-4.960	-5.578
-4.930	-5.517
-4.902	-5.499
-4.876	-5.461
-4.851	-5.425
-4.828	-5.394
-4.806	-5.365

Milli-Q Complexometric Titrations @ pH 7.5

Milli-Q Blank
Polypropylene

log [CuT]	log [CuF]
-7.000	-7.104
-6.523	-6.856
-6.301	-6.680
-6.165	-6.539
-6.046	-6.425
-5.959	-6.331
-5.887	-6.249
-5.825	-6.181
-5.771	-6.119
-5.722	-6.066
-5.679	-6.018
-5.640	-5.972
-5.603	-5.933
-5.570	-5.897
-5.539	-5.864
-5.510	-5.832
-5.483	-5.806
-5.458	-5.776
-5.434	-5.751
-5.411	-5.731
-5.389	-5.704
-5.369	-5.685
-5.349	-5.665
-5.330	-5.646
-5.312	-5.626
-5.295	-5.610
-5.278	-5.597
-5.262	-5.581
-5.247	-5.564
-5.232	-5.551
-5.218	-5.535
-5.204	-5.522
-5.190	-5.509
-5.177	-5.496
-5.164	-5.483
-5.152	-5.473
-5.140	-5.463
[illegible]	-5.447
-5.117	-5.437
-5.106	-5.427
-5.095	-5.417
-5.085	-5.408
-5.074	-5.398
-5.064	-5.391
-5.055	-5.378
-5.045	-5.369
-5.036	-5.362
-5.027	-5.355
-4.992	-5.326
-4.960	-5.290
-4.930	-5.258
-4.902	-5.228
-4.876	-5.205

log [CuT]	log [CuF]
-4.851	-5.179
-4.828	-5.157
-4.806	-5.137
-4.785	-5.114
-4.765	-5.095
-4.746	-5.088
-4.727	-5.072
-4.710	-5.055

Milli-Q Blank
Glass

Log [CuT]	Log [CuF]
-6.18795	-6.80266
-5.88695	-6.39791
-5.71088	-6.17343
-5.58597	-6.01697
-5.48909	-5.91493
-5.40993	-5.84011
-5.34301	-5.77208
-5.28505	-5.71426
-5.23392	-5.65984
-5.18819	-5.61903
-5.14683	-5.57821
-5.10907	-5.5442
-5.07433	-5.51019
-4.98391	-5.42856
-4.90936	-5.35713
-4.84577	-5.29251
-4.79034	-5.23809
-4.7412	-5.19727
-4.69708	-5.15646
-4.65704	-5.11904
-4.6204	-5.08503
-4.58662	-5.05782
-4.55529	-5.03061
-4.52609	-5.0068
-4.49873	-4.9864
-4.473	-4.96599
-4.44873	-4.94558
-4.42574	-4.93198
-4.40392	-4.91837
-4.38315	-4.90477
-4.36334	-4.89116
-4.3444	-4.88436
-4.32625	-4.87415
-4.30884	-4.87075
-4.29211	-4.86395
-4.276	-4.86055
-4.26048	-4.86055
-4.2455	-4.85715
-4.23102	-4.85375
-4.21701	-4.85375
-4.20345	-4.85375

Ideal Blank
@ pH 7.5

log [CuT]	log [CuF]
-7.000	-7.13629
-5.585	-5.73417
-5.293	-5.45304
-5.120	-5.29045
-4.996	-5.1769
-4.900	-5.0902
-4.821	-5.02041
-4.755	-4.96223
-4.697	-4.91248
-4.646	-4.86912
-4.601	-4.83078
-4.560	-4.79646
-4.522	-4.76543
-4.487	-4.73715
-4.455	-4.7112
-4.425	-4.7
-4.397	-4.7
-4.371	-4.7
-4.346	-4.7
-4.323	-4.7
-4.301	-4.7
-4.279	-4.7
-4.259	-4.7
-4.240	-4.7
-4.222	-4.7
-4.204	-4.7
-4.187	-4.7
-4.170	-4.7
-4.155	-4.7
-4.139	-4.7
-4.125	-4.7
-4.111	-4.7
-4.097	-4.7
-4.083	-4.7
-4.071	-4.7
-4.058	-4.7
-4.046	-4.7
-4.034	-4.7
-4.022	-4.7
-4.011	-4.7
-4.000	-4.7

Model Compounds Complexometric Titratons @ pH 7.5

Phthalic Acid
HEPES .0005M [L]=1.5E-4M

log [CuT]	log [CuF]	log [CuT]	log [CuF]
-6.700	-7.231	-4.668	-5.147
-6.399	-6.980	-4.638	-5.124
-6.223	-6.803	-4.610	-5.104
-6.098	-6.673		
-6.001	-6.565		
-5.922	-6.477		
-5.855	-6.402		
-5.797	-6.337		
-5.746	-6.275		
-5.700	-6.220		
-5.659	-6.171		
-5.621	-6.132		
-5.587	-6.093		
-5.555	-6.060		
-5.525	-6.027		
-5.497	-5.998		
-5.470	-5.969		
-5.446	-5.943		
-5.422	-5.916		
-5.400	-5.894		
-5.379	-5.871		
-5.359	-5.851		
-5.340	-5.832		
-5.321	-5.812		
-5.304	-5.796		
-5.287	-5.776		
-5.270	-5.760		
-5.255	-5.744		
-5.240	-5.727		
-5.225	-5.711		
-5.211	-5.698		
-5.197	-5.685		
-5.184	-5.672		
-5.171	-5.659		
-5.158	-5.646		
-5.146	-5.636		
-5.134	-5.623		
-5.123	-5.613		
-5.112	-5.600		
-5.101	-5.590		
-5.090	-5.581		
-5.080	-5.571		
-5.070	-5.561		
-5.060	-5.551		
-5.050	-5.541		
-5.005	-5.499		
-4.972	-5.460		
-4.941	-5.424		
-4.912	-5.395		
-4.860	-5.339		
-4.814	-5.290		
-4.772	-5.248		

Glycine
HEPES .0005 [L] 1E-5M

log [CuT]	log [CuF]
-6.097	-7.466
-5.921	-7.293
-5.796	-7.152
-5.700	-7.032
-5.621	-6.924
-5.554	-6.830
-5.496	-6.742
-5.445	-6.657
-5.399	-6.578
-5.358	-6.503
-5.321	-6.435
-5.286	-6.366
-5.254	-6.305
-5.224	-6.243
-5.196	-6.184
-5.170	-6.128
-5.146	-6.076
-5.122	-6.024
-5.100	-5.975
-5.079	-5.929
-5.059	-5.907
-5.013	-5.835
-4.979	-5.753
-4.948	-5.682
-4.919	-5.616
-4.891	-5.558
-4.866	-5.505
-4.842	-5.460
-4.819	-5.417

Glycine repeat
[L]=1E-5M HEPES .0

log [CuT]	log [CuF]
-6.398	-7.919
-6.222	-7.759
-6.097	-7.679
-6.000	-7.571
-5.921	-7.430
-5.854	-7.348
-5.796	-7.273
-5.745	-7.208
-5.700	-7.179
-5.678	-7.117
-5.639	-7.061
-5.603	-7.015
-5.570	-6.970
-5.539	-6.924
-5.510	-6.885
-5.483	-6.843
-5.457	-6.800
-5.433	-6.768
-5.410	-6.732
-5.389	-6.699
-5.368	-6.667
-5.348	-6.637
-5.330	-6.611
-5.312	-6.582
-5.294	-6.552
-5.278	-6.523
-5.262	-6.500
-5.246	-6.474
-5.231	-6.448
-5.217	-6.422
-5.203	-6.396
-5.190	-6.373
-5.177	-6.350
-5.164	-6.324
-5.152	-6.305
-5.140	-6.282
-5.128	-6.259
-5.117	-6.239
-5.105	-6.220
-5.095	-6.200
-5.084	-6.177
-5.074	-6.158
-5.064	-6.141
-5.054	-6.119
-5.045	-6.102
-5.035	-6.086
-5.026	-6.076
-4.992	-6.070
-4.959	-5.988
-4.930	-5.910
-4.902	-5.841
-4.851	-5.776

log [CuT]	log [CuF]
-4.727	-5.502
-4.693	-5.437
-4.661	-5.302
-4.632	-5.336
-4.604	-5.290
-4.579	-5.254
-4.554	-5.219
-4.532	-5.189
-4.510	-5.160
-4.489	-5.134
-4.470	-5.108
-4.451	-5.085

Salicylic Acid
HEPES=.005M [L] 1.13E-4M

log [CuT]	log [CuF]	log [CuT]	log [CuF]
-6.398	-7.678	-4.351	-5.353
-6.097	-7.356	-4.324	-5.320
-5.921	-7.154	-4.298	-5.284
-5.796	-7.014	-4.274	-5.252
-5.699	-6.903	-4.251	-5.219
-5.620	-6.815	-4.230	-5.193
-5.554	-6.740	-4.210	-5.164
-5.496	-6.672	-4.190	-5.141
-5.445	-6.616	-4.172	-5.118
-5.399	-6.564	-4.154	-5.092
-5.358	-6.522	-4.138	-5.073
-5.320	-6.476	-4.121	-5.050
-5.286	-6.437	-4.106	-5.030
-5.254	-6.405	-4.091	-5.014
-5.224	-6.369	-4.077	-5.001
-5.196	-6.340		
-5.170	-6.307		
-5.145	-6.281		
-5.111	-6.258		
-5.089	-6.232		
-5.069	-6.209		
-5.049	-6.200		
-5.031	-6.177		
-5.013	-6.157		
-4.995	-6.141		
-4.979	-6.125		
-4.963	-6.102		
-4.948	-6.086		
-4.933	-6.073		
-4.919	-6.056		
-4.905	-6.040		
-4.891	-6.024		
-4.878	-6.011		
-4.866	-5.998		
-4.854	-5.985		
-4.842	-5.968		
-4.830	-5.959		
-4.819	-5.949		
-4.808	-5.936		
-4.797	-5.926		
-4.787	-5.913		
-4.777	-5.903		
-4.767	-5.890		
-4.757	-5.871		
-4.739	-5.845		
-4.721	-5.822		
-4.687	-5.783		
-4.656	-5.740		
-4.627	-5.705		
-4.600	-5.677		
-4.574	-5.636		
-4.550	-5.607		
-4.527	-5.581		
-4.486	-5.529		
-4.449	-5.477		
-4.411	-5.431		

Catechol
HEPES=.005M [L]=4.989E-6M

log [CuT]	log [CuF]
-6.700	-8.612
-6.399	-8.341
-6.302	-7.949
-6.156	-7.703
-6.047	-7.466
-5.960	-7.310
-5.888	-7.171
-5.826	-7.032
-5.771	-6.939
-5.723	-6.821
-5.680	-6.737
-5.640	-6.640
-5.604	-6.567
-5.571	-6.491
-5.540	-6.428
-5.511	-6.376
-5.484	-6.341
-5.458	-6.289
-5.434	-6.255
-5.412	-6.213
-5.390	-6.192
-5.369	-6.171
-5.350	-6.137
-5.331	-6.078
-5.313	-6.039
-5.296	-6.005
-5.279	-5.987
-5.263	-5.953
-5.248	-5.946
-5.233	-5.907
-5.218	-5.894
-5.204	-5.897
-5.191	-5.838
-5.178	-5.841
-5.165	-5.828
-5.153	-5.803
-5.141	-5.782
-5.129	-5.758
-5.118	-5.741
-5.107	-5.734
-5.096	-5.723
-5.085	-5.706
-5.075	-5.703
-5.065	-5.689
-5.055	-5.671
-5.046	-5.668
-5.041	-5.675
-5.032	-5.668
-5.023	-5.650
-5.014	-5.598
-4.997	-5.505
-4.980	-5.435
-4.964	-5.397
-4.934	-5.317
-4.906	-5.280
-4.880	-5.200

Appendix B Titration Data of Model Mixture

POTENTIOMETRIC TITRATION OF OCGW XAD-8 MODEL MIXTURE

[NaOH]	Titrator MODEL MQ pH	Model OCGW-SAS pH	Actual Model Titration [NaOH]	Actual Model Titration pH
2.67E-05	2.96727	3.01618	7.97E-06	3
5.35E-05	2.97818	3.02822	1.59E-05	3.004
8.02E-05	2.98937	3.0406	2.15E-04	3.1
0.000107	3.00086	3.05334	3.81E-04	3.202
0.000134	3.01266	3.06645	5.07E-04	3.3
0.000161	3.02479	3.07998	5.62E-04	3.351
0.000187	3.03726	3.09393	6.09E-04	3.4
0.000214	3.05011	3.10833	6.56E-04	3.457
0.000241	3.06335	3.12323	6.95E-04	3.506
0.000268	3.077	3.13865	7.27E-04	3.555
0.000294	3.0911	3.15463	7.58E-04	3.61
0.000321	3.10567	3.17121	7.81E-04	3.657
0.000348	3.12075	3.18845	8.05E-04	3.709
0.000375	3.13637	3.20638	8.20E-04	3.747
0.000401	3.15257	3.22508	8.75E-04	3.919
0.000428	3.1694	3.24461	8.83E-04	3.95
0.000455	3.1869	3.26505	8.98E-04	4.021
0.000482	3.20515	3.28648	9.61E-04	4.499
0.000508	3.22419	3.30901	9.92E-04	4.975
0.000535	3.24411	3.33275	1.01E-03	5.529
0.000562	3.26498	3.35785	1.02E-03	5.843
0.000589	3.28691	3.38446	1.03E-03	6.531
0.000615	3.31001	3.41279	1.04E-03	8.334
0.000642	3.3344	3.44306	1.05E-03	8.767999
0.000669	3.36024	3.47555	1.05E-03	8.998999
0.000696	3.38772	3.51063	1.07E-03	9.281
0.000722	3.41706	3.54872	1.09E-03	9.534001
0.000749	3.44852	3.59039	1.10E-03	9.596
0.000776	3.48244	3.63642	1.11E-03	9.649999
0.000803	3.51923	3.68772	1.12E-03	9.699001
0.000829	3.55944	3.74565	1.12E-03	9.744001
0.000856	3.60374	3.81214	1.13E-03	9.783
0.000883	3.65307	3.89	1.14E-03	9.819
0.00091	3.70882	3.98365	1.15E-03	9.852999
0.000936	3.77272	4.10036	1.16E-03	9.915
0.000963	3.84767	4.25285	1.18E-03	9.967
0.00099	3.93831	4.46408	1.19E-03	9.991
0.001017	4.053	4.77284	1.19E-03	10.014
0.001043	4.20926	5.25762		
0.00107	4.4558	8.21701		
0.001097	5.0829	9.28201		
0.001124	9.26697	9.61777		
0.00115	9.65553	9.81881		
0.001177	9.85728	9.9602		
0.001204	9.9945	10.0685		

OCGW Model and Model Titration @ pH 6.2

Model of OCGW @ pH 6.2 log [CuT]	log [CuF]	Actual Model Titration log [CuT]	log [CuF]	Actual Model Titration log [CuT]	log [CuF]
-7	-7.44448	-7.000	-7.883	-5.064	-5.560
-6.03152	-6.47197	-6.523	-7.463	-5.054	-5.553
-5.75449	-6.19098	-6.301	-7.196	-5.045	-5.546
-5.5867	-6.01932	-6.155	-6.998	-5.036	-5.546
-5.46597	-5.89479	-6.046	-6.859	-5.031	-5.543
-5.37161	-5.7967	-5.959	-6.748	-4.992	-5.498
-5.29414	-5.71558	-5.887	-6.647	-4.959	-5.453
-5.22841	-5.64627	-5.825	-6.574	-4.930	-5.428
-5.17134	-5.58568	-5.770	-6.519	-4.902	-5.376
-5.1209	-5.5318	-5.722	-6.435	-4.851	-5.331
-5.07572	-5.48323	-5.679	-6.369	-4.805	-5.269
-5.0348	-5.43899	-5.639	-6.317	-4.764	-5.209
-4.9974	-5.39833	-5.603	-6.269	-4.727	-5.164
-4.96297	-5.36071	-5.570	-6.227	-4.693	-5.119
-4.93107	-5.32567	-5.539	-6.185	-4.632	-5.043
-4.90136	-5.29287	-5.510	-6.137	-4.579	-4.963
-4.87354	-5.26203	-5.483	-6.109	-4.532	-4.904
-4.84741	-5.23292	-5.457	-6.071	-4.489	-4.848
-4.82275	-5.20535	-5.433	-6.046	-4.451	-4.793
-4.79942	-5.17915	-5.411	-6.039		
-4.77728	-5.15419	-5.389	-6.001		
-4.75622	-5.13035	-5.368	-5.980		
-4.73613	-5.10754	-5.349	-5.932		
-4.71693	-5.08566	-5.330	-5.911		
-4.69854	-5.06464	-5.312	-5.876		
-4.68089	-5.04441	-5.295	-5.887		
-4.66394	-5.02491	-5.278	-5.852		
-4.64762	-5.00609	-5.262	-5.821		
-4.6312	-4.9879	-5.247	-5.786		
-4.61672	-4.9703	-5.232	-5.769		
-4.60206	-4.95324	-5.217	-5.762		
		-5.203	-5.755		
		-5.190	-5.748		
		-5.177	-5.734		
		-5.164	-5.706		
		-5.152	-5.689		
		-5.140	-5.668		
		-5.128	-5.654		
		-5.117	-5.640		
		-5.106	-5.626		
		-5.095	-5.616		
		-5.085	-5.605		
		-5.074	-5.588		

Appendix C Titration Data of Natural Sources

Potentiometric Titration of OCGW XAD-8

(by W. Odem & J. Taylor)

Milli-Q Blank [NaOH]	pH	DOC = 5.66 mg/L OCGW XAD-8 [NaOH]	pH
1.15E-05	3.002	2.31E-05	3.003
5.97E-05	3.022	6.92E-05	3.022
1.04E-04	3.043	1.04E-04	3.035
1.50E-04	3.065	1.50E-04	3.056
2.07E-04	3.092	2.07E-04	3.082
2.53E-04	3.114	2.53E-04	3.104
2.99E-04	3.139	3.11E-04	3.132
3.56E-04	3.171	3.33E-04	3.145
4.02E-04	3.199	3.68E-04	3.163
4.59E-04	3.235	4.36E-04	3.203
5.05E-04	3.267	4.71E-04	3.224
5.50E-04	3.301	5.39E-04	3.269
6.07E-04	3.349	5.73E-04	3.293
6.53E-04	3.389	6.30E-04	3.336
7.10E-04	3.447	6.87E-04	3.385
7.55E-04	3.5	7.32E-04	3.428
8.00E-04	3.56	7.89E-04	3.489
8.57E-04	3.65	8.34E-04	3.542
9.02E-04	3.738	8.79E-04	3.606
9.58E-04	3.881	9.36E-04	3.698
1.00E-03	4.041	9.81E-04	3.79
1.05E-03	4.298	1.03E-03	3.895
1.07E-03	4.523	1.08E-03	4.077
1.08E-03	4.698	1.13E-03	4.319
1.09E-03	4.986	1.14E-03	4.405
1.10E-03	5.848	1.17E-03	4.817
1.12E-03	8.798001	1.18E-03	5.078
1.13E-03	9.245	1.19E-03	5.558
1.14E-03	9.472999	1.21E-03	6.568
1.15E-03	9.627	1.22E-03	7.712
1.17E-03	9.838	1.23E-03	8.559
1.19E-03	9.983	1.24E-03	8.897001
1.22E-03	10.093	1.25E-03	9.100001
1.22E-03	10.09	1.26E-03	9.252
1.23E-03	10.128	1.27E-03	9.371
1.24E-03	10.128	1.28E-03	9.477
1.23E-03	10.125	1.29E-03	9.564
1.23E-03	10.124	1.31E-03	9.639
1.23E-03	10.12	1.32E-03	9.708
1.23E-03	10.12	1.34E-03	9.829001
1.23E-03	10.118	1.36E-03	9.929
1.23E-03	10.118	1.37E-03	9.976
1.23E-03	10.116	1.39E-03	10.055

OCGW XAD-8 Complexometric Titrations @ pH 6.2
----------(after Waterbury, 1990)-------------

OCGW XAD-8 log [CuT]	log [CuF]	Repeat log [CuT]	log [CuF]	(Castro) Corrected for Milli-Q Blank log [CuT]	log [CuF]
-6.60217	-9.35777	-6.60206	-9.14829	-5.46597	-6.80693
-6.30125	-9.01557	-6.60114	-8.80608	-5.37161	-6.74058
-6.12526	-8.73855	-6.12516	-8.57795	-5.29414	-6.60931
-6.00043	-8.52671	-6.00033	-8.38783	-5.22841	-6.43878
-5.90363	-8.35154	-5.90352	-8.23574	-5.17134	-6.25661
-5.82456	-8.2008	-5.82445	-8.12167	-5.1209	-6.09253
-5.75772	-8.07044	-5.75761	-8.0076	-5.07572	-5.95679
-5.69984	-7.95637	-5.69973	-7.89354	-5.0348	-5.84512
-5.64879	-7.84638	-5.60293	-7.70342	-4.9974	-5.75107
-5.60314	-7.74046	-5.52396	-7.51331	-4.96297	-5.66965
-5.56186	-7.64269	-5.45723	-7.32319	-4.93107	-5.59753
-5.52418	-7.54899	-5.39946	-7.20913	-4.90136	-5.5325
-5.48953	-7.45937	-5.34852	-7.05703	-4.87354	-5.47303
-5.45745	-7.37789	-5.30298	-6.94297	-4.84741	-5.41809
-5.42759	-7.29234	-5.2618	-6.8289	-4.82275	-5.36692
-5.39967	-7.21086	-5.22423	-6.71483	-4.79942	-5.31901
-5.37345	-7.12938	-5.18968	-6.60076	-4.77728	-5.27391
-5.34874	-7.05198	-5.12775	-6.41065	-4.75622	-5.23136
-5.32536	-6.97865	-5.07383	-6.25856	-4.73613	-5.19109
-5.3032	-6.9094	-5.02595	-6.14449	-4.71693	-5.15292
-5.28212	-6.84014	-4.9727	-5.9924	-4.69854	-5.11666
-5.26202	-6.77089	-4.92546	-5.87833	-4.68089	-5.08221
-5.24282	-6.7057	-4.88297	-5.80228	-4.66394	-5.04941
-5.22445	-6.6446	-4.84435	-5.68821	-4.64762	-5.01817
-5.20683	-6.58349	-4.80897	-5.61217	-4.6319	-4.98839
-5.1899	-6.52646	-4.77634	-5.57414	-4.61672	-4.95996
-5.17362	-6.47349			-4.60206	-4.93282
-5.15793	-6.42054				
-5.1428	-6.37165				
-5.12818	-6.31869				
-5.11405	-6.27388				
-5.10037	-6.22907				
-5.08711	-6.18833				
-5.07426	-6.14759				
-5.06177	-6.11092				
-5.04965	-6.07426				
-5.03208	-6.03759				
-5.00973	-5.97241				
-4.9885	-5.90723				
-4.96827	-5.84612				
-4.94896	-5.79317				
-4.93049	-5.73613				
-4.9128	-5.69539				
-4.89581	-5.64651				
-4.87948	-5.60577				
-4.86375	-5.56503				
-4.84859	-5.52836				
-4.83396	-5.48763				
-4.81991	-5.45911				
-4.80613	-5.42652				

'OCGW XAD-8 PH 7.5 COMPLEXOMETRIC TITRATION'

log [CuT]	log [CuF]
-5.28505	-6.87068
-5.18819	-6.68702
-5.10907	-6.54757
-5.04217	-6.43192
-4.98424	-6.34349
-4.93314	-6.26526
-4.88744	-6.19384
-4.8461	-6.13261
-4.80836	-6.0816
-4.77365	-6.03738
-4.74152	-5.99316
-4.71161	-5.96255
-4.68364	-5.92854
-4.65737	-5.89453
-4.6326	-5.87752
-4.60917	-5.85711
-4.58695	-5.8333
-4.56581	-5.8095
-4.54566	-5.79249
-4.52641	-5.77548
-4.50798	-5.75848
-4.49031	-5.74147
-4.47333	-5.72787
-4.45699	-5.71426
-4.44125	-5.69725
-4.42607	-5.68365
-4.4114	-5.68025
-4.39721	-5.66664
-4.38348	-5.65304
-4.37017	-5.64283
-4.35726	-5.62923
-4.34472	-5.61562
-4.33254	-5.60542
-4.32069	-5.59182
-4.30917	-5.58161
-4.29794	-5.56801
-4.287	-5.5578
-4.27633	-5.5578
-4.26592	-5.5476
-4.25575	-5.5374
-4.24582	-5.52379
-4.23612	-5.51699
-4.22662	-5.50679
-4.20825	-5.47277
-4.19063	-5.44556
-4.1737	-5.42516
-4.15742	-5.40815
-4.14173	-5.40475
-4.1266	-5.38774
-4.11199	-5.37414
-4.09785	-5.36393
-4.08417	-5.35033
-4.07092	-5.33672
-4.05906	-5.32652
-4.04558	-5.31632
-4.03345	-5.30951
-4.02166	-5.29931

log [CuT]	log [CuF]
-4.01019	-5.28911
-3.99901	-5.2857
-3.98812	-5.2755
-3.97751	-5.2687
-3.96715	-5.2653
-3.95704	-5.2687
-3.94716	-5.2755
-3.93751	-5.2653
-3.92807	-5.25169
-3.91884	-5.24829
-3.9098	-5.23809
-3.90095	-5.23128
-3.89229	-5.22448
-3.88379	-5.21768
-3.87547	-5.21428
-3.8673	-5.20407
-3.85929	-5.19727
-3.85143	-5.19387

Potentiometric Titration of PA XAD-8

(by W. Odem & J. Taylor)

Milli-Q Blank [NaOH]	pH	DOC-12.66 mg/L PA XAD-8 [NaOH]	pH
1.15E-05	3.002	1.15E-05	2.996
2.31E-05	3.007	2.31E-05	3.001
3.46E-05	3.011	3.46E-05	3.005
4.62E-05	3.017	4.62E-05	3.009
5.77E-05	3.022	5.77E-05	3.013
6.92E-05	3.027	6.92E-05	3.018
8.08E-05	3.032	8.08E-05	3.022
9.23E-05	3.037	9.23E-05	3.026
0.000104	3.043	0.000104	3.031
0.000115	3.048	0.000115	3.036
0.000127	3.054	0.000127	3.041
0.000138	3.059	0.000138	3.046
0.00015	3.065	0.00015	3.05
0.000161	3.07	0.000161	3.054
0.000173	3.074	0.000173	3.059
0.000184	3.08	0.000184	3.065
0.000196	3.087	0.000196	3.07
0.000207	3.092	0.000207	3.075
0.000219	3.097	0.000219	3.081
0.00023	3.103	0.00023	3.086
0.000242	3.109	0.000242	3.092
0.000253	3.114	0.000253	3.098
0.000265	3.121	0.000265	3.104
0.000276	3.127	0.000276	3.109
0.000288	3.133	0.000288	3.115
0.000299	3.139	0.000299	3.121
0.000311	3.146	0.000311	3.128
0.000322	3.151	0.000322	3.132
0.000333	3.158	0.000333	3.139
0.000345	3.164	0.000345	3.145
0.000356	3.171	0.000356	3.15
0.000368	3.178	0.000368	3.156
0.000379	3.184	0.000379	3.161
0.000391	3.191	0.000391	3.169
0.000402	3.199	0.000402	3.173
0.000414	3.206	0.000414	3.18
0.000425	3.214	0.000425	3.187
0.000436	3.22	0.000436	3.195
0.000448	3.228	0.000448	3.203
0.000459	3.235	0.000459	3.211
0.000471	3.243	0.000471	3.219
0.000482	3.251	0.000482	3.226
0.000493	3.259	0.000493	3.234
0.000505	3.267	0.000505	3.243
0.000516	3.275	0.000516	3.252
0.000528	3.284	0.000528	3.26
0.000539	3.292	0.000539	3.269
0.00055	3.301	0.00055	3.278
0.000562	3.31	0.000562	3.287
0.000573	3.32	0.000573	3.297
0.000585	3.329	0.000585	3.307
0.000596	3.338	0.000596	3.317
0.000607	3.349	0.000607	3.327

Potentiometric Titration of BA XAD-8

(by W. Odem & J. Taylor)

Milli-Q Blank [NaOH]	pH	DOC=12.66 mg/L BA XAD-8 [NaOH]	pH
0.000619	3.358	0.000619	3.337
0.00063	3.369	0.00063	3.348
0.000641	3.378	0.000641	3.359
0.000653	3.389	0.000653	3.37
0.000664	3.4	0.000664	3.382
0.000675	3.412	0.000675	3.392
0.000687	3.424	0.000687	3.405
0.000698	3.435	0.000698	3.417
0.00071	3.447	0.00071	3.43
0.000721	3.46	0.000721	3.443
0.000732	3.473	0.000732	3.457
0.000744	3.487	0.000744	3.471
0.000755	3.5	0.000755	3.485
0.000766	3.515	0.000766	3.5
0.000777	3.529	0.000777	3.516
0.000789	3.544	0.000789	3.53
0.0008	3.56	0.0008	3.547
0.000811	3.577	0.000811	3.564
0.000823	3.594	0.000823	3.582
0.000834	3.611	0.000834	3.6
0.000845	3.631	0.000845	3.619
0.000857	3.65	0.000857	3.638
0.000868	3.67	0.000868	3.658
0.000879	3.692	0.000879	3.68
0.00089	3.715	0.00089	3.702
0.000902	3.738	0.000902	3.725
0.000913	3.763	0.000913	3.75
0.000924	3.79	0.000924	3.775
0.000936	3.817	0.000936	3.802
0.000947	3.849	0.000947	3.831
0.000958	3.881	0.000958	3.86
0.000969	3.916	0.000969	3.892
0.000981	3.954	0.000981	3.925
0.000992	3.996	0.000992	3.96
0.001003	4.041	0.001003	3.998
0.001014	4.093	0.001014	4.037
0.001026	4.152	0.001026	4.079
0.001037	4.22	0.001037	4.125
0.001048	4.298	0.001048	4.174
0.001059	4.398	0.001059	4.226
0.001071	4.523	0.001071	4.283

Potentiometric Titration of BA XAD-8

(by W. Odem & J. Taylor)

Milli-Q Blank [NaOH]	pH	DOC: 12.66 mg/L BA XAD-8 [NaOH]	pH
0.001082	4.698	0.001082	4.344
0.001093	4.986	0.001093	4.41
0.001104	5.848	0.001104	4.484
0.001116	8.798001	0.001116	4.563
0.001127	9.245	0.001127	4.649
0.001138	9.472999	0.001138	4.745
0.001149	9.627	0.001149	4.849
0.00116	9.745	0.00116	4.964
0.001172	9.838	0.001172	5.09
0.001183	9.916001	0.001183	5.235
0.001194	9.983	0.001194	5.398
0.001205	10.042	0.001205	5.584
0.001216	10.093	0.001216	5.807
0.001216	10.092	0.001228	6.077
0.001216	10.091	0.001239	6.421
0.001216	10.09	0.00125	6.893
0.001216	10.09	0.001261	7.542
0.001216	10.088	0.001272	8.222
0.001228	10.128	0.001283	8.665
0.001228	10.128	0.001295	8.943
0.001228	10.128	0.001306	9.142999
0.001228	10.127	0.001317	9.295
0.001228	10.126	0.001328	9.417
0.001228	10.125	0.001339	9.521
0.001228	10.125	0.00135	9.612001
0.001228	10.124	0.001361	9.692001
0.001228	10.124	0.001373	9.762999
0.001228	10.122	0.001384	9.829001
0.001228	10.121	0.001395	9.887
0.001228	10.12	0.001406	9.939999
0.001228	10.12	0.001417	9.989001
0.001228	10.118	0.001428	10.032

'BISCAYNE AQUIFER XAD-8 PH 6.2 COMPLEXOMETRIC TITRATION'

log [CuT]	log [CuF]
-5.784	-6.989
-5.711	-6.887
-5.649	-6.798
-5.595	-6.714
-5.504	-6.496
-5.464	-6.442
-5.428	-6.360
-5.395	-6.221
-5.364	-6.170
-5.335	-6.109
-5.308	-6.011
-5.283	-5.997
-5.259	-5.943
-5.236	-5.882
-5.214	-5.807
-5.194	-5.770
-5.174	-5.749
-5.155	-5.719
-5.137	-5.675
-5.120	-5.627
-5.104	-5.596
-5.088	-5.563
-5.072	-5.532
-5.057	-5.505
-5.043	-5.484
-5.022	-5.474
-5.009	-5.464
-4.984	-5.413
-4.960	-5.383
-4.937	-5.332
-4.916	-5.291
-4.876	-5.243
-4.840	-5.209
-4.775	-5.050
-4.719	-4.958
-4.670	-4.887

'BISCAYNE AQUIFER XAD-8 PH 7.5 COMPLEXOMETRIC TITRATION'

log [CuT]	log [CuF]
-5.428	-6.942
-5.395	-6.866
-5.364	-6.773
-5.335	-6.732
-5.308	-6.649
-5.283	-6.590
-5.259	-6.507
-5.236	-6.473
-5.215	-6.417
-5.194	-6.359
-5.174	-6.321
-5.156	-6.269
-5.138	-6.255
-5.120	-6.207
-5.104	-6.196
-5.088	-6.138
-5.073	-6.110
-5.058	-6.096
-5.043	-6.069
-5.023	-6.062
-5.009	-6.055
-4.984	-5.996
-4.960	-5.937
-4.938	-5.896
-4.916	-5.858
-4.876	-5.761
-4.840	-5.733
-4.806	-5.702
-4.746	-5.626
-4.694	-5.547
-4.647	-5.533
-4.605	-5.512
-4.567	-5.499
-4.532	-5.464
-4.500	-5.450
-4.470	-5.436
-4.443	-5.385
-4.417	-5.333
-4.392	-5.305
-4.369	-5.281
-4.327	-5.219
-4.289	-5.198
-4.254	-5.146
-4.222	-5.098
-4.193	-5.063

Appendix D Computer Programs

BASIC PROGRAM FOR POTENTIOMETRIC TITRATIONS

```
10      TL = .01
15      INPUT "OUTPUT FILE NAME (****.dat) =>";FILE$
20      INPUT "ENTER EXPERIMENT ID =>";ID$
30      INPUT "ENTER pH SET POINT =>";SPH
40      INPUT "ENTER PRINT INTERVAL IN MINUTES->";PI
41      INPUT "ALIQUOT SIZE FOR ACID";M1
42      INPUT "STRENGTH OF ACID IN (M) =>";C1
43      INPUT "ALIQUOT SIZE FOR BASE =>";M2
44      INPUT "STRENGTH OF BASE IN (M)=>";C2
45      INPUT "pH TOLERANCE =>";TL
46      ACD = M1 * .00025 * C1 / 1000!
47      BAS = M2 * .00025 * C2 / 1000!
50      D$ = CHR$(4)
55      W$ = CHR$(23)
60      PRINT D$:OPEN "lpt1:" FOR OUTPUT AS #1
61      PRINT #1,"EXPERIMENT ID,FILE and DATE =";ID$,FILE$,DATE$
62      PRINT #1,"MOLE OF ACID PER ADDITION =";ACD
63      PRINT #1,"MOLE OF BASE PER ADDITION =";BAS
64      PRINT #1,"pH TOLERANCE =";TL
65      PRINT #1,"SET POINT pH =";SPH
66      PRINT #1,:PRINT #1,:PRINT #1,:PRINT #1,
67      PRINT #1,"TIME(SEC)       #ACID       #BASE        #pH"
68      PRINT #1,"------------------------------------------"
69      PRINT D$:CLOSE #1
70      OPEN FILE$ FOR OUTPUT AS #2
71      PRINT #2, "EXPERIMENT ID and FILE ==> ";ID$,FILE$
72      PRINT #2, "DATE OF EXPERIMENT ==> ";DATE$
73      PRINT #2, "MOLES OF ACID PER ADDITION ==> ";ACD
74      PRINT #2, "MOLES OF BASE PER ADDITION ==> ";BAS
75      PRINT #2, "pH SET POINT ==> ";SPH
76      PRINT #2, "pH TOLERANCE ==> ";TL
77      PRINT #2,"time","#acid","#base","pH"
78      CLOSE #2
140     GOSUB 2000
150     GOSUB 3000
160     TO = MIN + SEC / 60 + HR * 60
170     GOSUB   6000
180     CLS
190     GOSUB 5000
192     K = PEEK(1048) AND 128
194     IF K = 128 THEN GOSUB 8000
196     IF FI = 0 GOTO 140
197     GOSUB 2000
198     DF = ABS(SPH-PH)
210     IF (PH - SPH) > = TL THEN GOSUB 4000
215     IF (SPH - PH) > = TL THEN GOSUB 10000
220     GOSUB 3000
235     TIME = MIN + SEC/60 +HR*60
240     IF (TIME - TO) < PI GOTO 280
260     GOSUB 6000
270     TO = TIME
280     GOSUB 5000
290     GOTO 192
2000    PRINT D$:OPEN "COM1:600,s,7,2,CS,DS,CD" FOR INPUT AS #2
2005    LOCATE 24,1
2010     INPUT #2, PH$: CLOSE #2
2015    CLS
2020    PRINT D$
2030    PH = VAL(LEFT$(PH$,7))
2035    PH = INT(PH*1000 + .5)/1000
```

```
2036    IF PH >= SPH THEN GOTO 10080
2040    RETURN
3000    T$ = TIME$
3045    HR = VAL(MID$(T$,1,2))
3060    MIN = VAL(MID$(T$,4,2))
3070    SEC = VAL(MID$(T$,7,2))
3072    IF F1 < > 0 GOTO 3078
3074    IHR = HR:IMIN = MIN
3075    ISEC = SEC
3076    F1 = 1
3078    IF SEC > = ISEC GOTO 3082
3080    MIN = MIN - 1:SEC = 60 + SEC - ISEC
3081    GOTO 3084
3082    SEC = SEC - ISEC
3084    IF MIN > = IMIN GOTO 3088
3086    HR = HR - 1:MIN = 60 +MIN  - IMIN
3087    GOTO 3090
3088    MIN = MIN - IMIN
3090    GOSUB 9100
3095    O$ = RIGHT$(T$,8):D7$ = LEFT$(T$,11)
3100    RETURN
4000    OUT DDRB,136
4005    FOR I = 1 TO N1
4010    OUT PB,1
4020    JJ = 0
4030    OUT PB,0
4040    NEXT I
4045    AC=AC + 1
4050    RETURN
5000    CLS
5005    PRINT D7$
5010    LOCATE 10,1
5020    PRINT "  pH        ELAPSED TIME    TIME      #ADD"
5030    PRINT
5035    TS = TIME * 60!
5040    PRINT PH; TAB(13);HR;":";MIN;":";SEC;TAB(26);O$
5050    LOCATE 12,36: PRINT AC;"/";AB
5055    LOCATE 20,1
5056    PRINT "TO INTERRUPT THE PROGRAM: PRESS 'Ins' key (num lock light must be
 off!) RELEASE KEY ONLY AFTER MENU APPEARS"
5060    RETURN
6000    PRINT D$:OPEN "lpt1:" AS #1
6003    IF F1 < > 0 GOTO 6010
6004    PRINT #1,: PRINT #1,: PRINT #1,: PRINT #1, D$:PRINT #1,: PRINT #1,
6005    PRINT #1," pH          ELPSD T TIME          #ADD"
6007    F1 = 1: PRINT #1,
6010    PRINT #1,TS; TAB(15);AC; TAB(25);AB; TAB(35); PH
6020    PRINT #1, D$: CLOSE #1
6025    OPEN FILE$ FOR APPEND AS #2
6026    PRINT#2, TS,AC,AB,PH
6027    CLOSE#2
6030    RETURN
7000    PRINT D$:OPEN "LPT1:" AS #1
7010    PRINT #1,:PRINT #1,
7020    PRINT #1,D7$
7030    PRINT #1,: PRINT #1,: PRINT #1,D$: CLOSE #1
7040    RETURN
8000    K=0:CLS:COLOR 0,7
8010    PRINT "PARAMETER CHANGE MENU":PRINT:PRINT
8015    PRINT "1) FILL/EMPTY SYRINGE"
```

```
8020     PRINT "2) SET POINT pH"
8030     PRINT "3) SET PRINT INTERVAL"
8040     PRINT "4) RESET ELAPSED TIME"
8050     PRINT "5) RESET ALIQUOT SIZE"
8060     PRINT "6) RETURN TO PROGRAM"
8070     PRINT "7) EXIT"
8075     PRINT "8) SET TOLERANCE"
8080     PRINT: INPUT "ENTER THE NUMBER OF YOUR CHOICE =>";K9
8081     OPEN FILE$ FOR APPEND AS #2
8082     PRINT #2, "CHANGE #";K9
8083     CLOSE #2
8084     CLS:COLOR 7,0
8085     IF K9 = 6 THEN RETURN
8090     ON K9 GOSUB 8300,8130,8150,8170,8180,8120,8200,8220
8100     GOTO 8000
8120     RETURN
8130     INPUT "ENTER pH SET POINT =>";SPH
8140     RETURN
8150     INPUT "ENTER PRINT INTERVAL IN MINUTES =>";PI
8160     RETURN
8170     INPUT "ENTER NUMBER OF ELAPSED DAYS =>";DAY
8172     INPUT "ENTER INITIAL HOUR =>";IHR
8173     INPUT "ENTER INITIAL MINUTES =>";MIN
8174     INPUT "ENTER INITIAL SECONDS =>";ISEC
8175     RETURN
8180     INPUT "ENTER ALIQUOT SIZE FOR ACID";M1
8190     RETURN
8200     COLOR 7,0:END
8220     INPUT "ENTER TOLERANCE IN pH UNITS =>";TL
8230     RETURN
8300     M=200
8400     OUT DDRB,136
8430     PRINT "EMPTY(1)   FILL(2)"
8440     INPUT N
8441     IF N=1 THEN GOTO 8445
8442     IF N=2 THEN GOTO 8545
8443     RETURN
8445     FOR I=1 TO M
8450     OUT PB,1
8460     J=0
8470     OUT PB,0
8480     NEXT I
8490     GOTO 8430
8545     FOR I=1 TO M
8550     OUT PB,3
8560     J=0
8570     OUT PB,2
8580     NEXT I
8590     GOTO 8430
9100     IF HR > = IHR GOTO 9160
9110     IF F3 = 1 GOTO 9170
9120     DAY = DAY + 1
9140     F3 = 1
9150     GOTO 9170
9160     F3 = 0
9170     HR = HR + DAY*24 - IHR
9180     RETURN
10000    OUT DDRB,136
10005 PRINT "**********************************************"
10010    FOR I = 1 TO M2
```

```
10015  JJ = 0
10020  OUT PB,1
10030  JJ = 0
10040  OUT PB,0
10050  NEXT I
10060  AB = AB + 1
10070  RETURN
10080  END
10010  FOR I = 1 TO M2
10015  JJ = 0
10020  OUT PB,1
10030  JJ = 0
10040  OUT PB,0
10050  NEXT I
10060  AB = AB + 1
10070  RETURN
10080  END
```

BASIC PROGRAM FOR COMPLEXOMETRIC TITRATION

```
1       DEF SEG = 0: CLS : :F1 = 0:F3 = 0:DAY = 0
2       N = 10:29 = - 16384
3       DDPB = 547:AC = 0
4       PB = 544
5       AB = 0
10      TL = 0
15      INPUT "OUTPUT FILE NAME =>";FILE$
20      INPUT "ENTER EXPERIMENT ID =>";ID$
30      INPUT "ENTER NUMBER OF COPPER SOLUTION ADDITIONS =>";SPH
35      INPUT "ENTER PRINT INTERVAL IN MINUTES=>";PI
41      INPUT "ALIQUOT SIZE FOR COPPER SOLUTION";M1
42      INPUT "CONCENTRATION OF COPPER IN (M) =>";C1
45      ACD = M1 * .00025 * C1 / 1000!
50      D$ = CHR$(4)
55      W$ = CHR$(23)
60      PRINT D$:OPEN "lpt1:" FOR OUTPUT AS #1
61      PRINT #1,"EXPERIMENT ID,FILE and DATE =";ID$,FILE$,DATE$
62      PRINT #1,"MOLES OF COPPER PER ADDITION =";ACD
65      PRINT #1,"NUMBER OF COPPER SOLUTION ADDITIONS =";SPH
66      PRINT #1,:PRINT #1,:PRINT #1,:PRINT #1,
67      PRINT #1,"TIME(SEC)        #COPPER SOLUTION       #MV"
68      PRINT #1,"-------------------------------------------"
69      PRINT D$:CLOSE #1
70      OPEN FILE$ FOR OUTPUT AS #2
71      PRINT #2, "EXPERIMENT ID and FILE ==> ";ID$,FILE$
72      PRINT #2, "DATE OF EXPERIMENT ==> ";DATE$
73      PRINT #2, "MOLES OF COPPER PER ADDITION ==> ";ACD
75      PRINT #2, "NUMBER OF COPPER SOLUTION ADDITIONS ==> ";SPH
77      PRINT #2,"time","# COPPER SOLUTION","MV"
78      CLOSE #2
140     GOSUB 2000
150     GOSUB 3000
160     TO = MIN + SEC / 60 + HR * 60
170     GOSUB   6000
180     CLS
190     GOSUB 5000
192     K = PEEK(1048) AND 128
193     IF K = 128 THEN GOSUB 8000
195     IF F1 = 0 GOTO 140
197     GOSUB 2000
200     GOSUB 4000
220     GOSUB 3000
235     TIME = MIN + SEC/60 +HR*60
240     IF (TIME - TO) < PI GOTO 280
260     GOSUB 6000
270     TO = TIME
280     GOSUB 5000
290     GOTO 192
2000    PRINT D$:OPEN "COM1:600,s,7,2,CS,DS,CD" FOR INPUT AS #2
2005    LOCATE 24,1
2010     INPUT #2, MV$: CLOSE #2
2015    CLS
2020    PRINT D$
2030    MV = VAL(LEFT$(MV$,7))
2031    MV = INT(MV*1000 + .5)/1000
2035    RETURN
3000    T$ = TIME$
3015    HR = VAL(MID$(T$,1,2))
3020    MIN = VAL(MID$(T$,4,2))
3025    SEC = VAL(MID$(T$,7,2))
```

```
3072    IF F1 < > 0 GOTO 3078
3074    IHR = HR:IMIN = MIN
3075    ISEC = SEC
3076    F1 = 1
3078    IF SEC > = ISEC GOTO 3082
3080    MIN = MIN - 1:SEC = 60 + SEC - ISEC
3081    GOTO 3084
3082    SEC = SEC - ISEC
3084    IF MIN > = IMIN GOTO 3088
3086    HR = HR - 1:MIN = 60 +MIN  - IMIN
3087    GOTO 3090
3088    MIN = MIN - IMIN
3090    GOSUB 9100
3095    O$ = RIGHT$(T$,8):D7$ = LEFT$(T$,11)
3100    RETURN
4000    IF TL >= SPH THEN GOTO 10020
4001    OUT DDRB,136
4005    FOR I = 1 TO M1
4010    OUT PB,1
4020    JJ = 0
4030    OUT PB,0
4040    NEXT I
4045    AC=AC + 1
4046    TL = TL + 1
4050    RETURN
5000    CLS
5005    PRINT D7$
5010    LOCATE 10,1
5020    PRINT "  MV        ELAPSED TIME     TIME      #ADD"
5030    PRINT
5035    TS = TIME * 60!
5040    PRINT MV; TAB(13);HR;":";MIN;":";SEC;TAB(26);O$
5050    LOCATE 12,36: PRINT AC;"/";AB
5055    LOCATE 20,1
5056    PRINT "TO INTERRUPT THE PROGRAM: PRESS 'Ins' key (num lock light must be
 off!) RELEASE KEY ONLY AFTER MENU APPEARS"
5060    RETURN
6000    PRINT D$:OPEN "lpt1:" AS #1
6003    IF F1 < > 0 GOTO 6010
6004    PRINT #1,: PRINT #1,: PRINT #1,: PRINT #1, D$:PRINT #1,: PRINT #1,
6005    PRINT #1," MV        ELPSD T TIME         #ADD"
6007    F1 = 1: PRINT #1,
6010    PRINT #1,TS; TAB(25);AC; TAB(35); MV
6020    PRINT #1, D$: CLOSE #1
6025    OPEN FILE$ FOR APPEND AS #2
6026    PRINT#2, TS,AC,MV
6027    CLOSE#2
6030    RETURN
7000    PRINT D$:OPEN "LPT1:" AS #1
7010    PRINT #1,:PRINT #1,
7020    PRINT #1,D7$
7030    PRINT #1,: PRINT #1,: PRINT #1,D$: CLOSE #1
7040    RETURN
8000    K=0:CLS:COLOR 0,7
8010    PRINT "PARAMETER CHANGE MENU":PRINT:PRINT
8015    PRINT "1) FILL/EMPTY SYRINGE"
8020    PRINT "2) NUMBER OF COPPER SOLUTION ADDITIONS"
8030    PRINT "3) SET PRINT INTERVAL"
8040    PRINT "4) RESET ELAPSED TIME"
8050    PRINT "5) RESET ALIQUOT SIZE"
```

```
8060    PRINT "6) RETURN TO PROGRAM"
8070    PRINT "7) EXIT"
8080    PRINT: INPUT "ENTER THE NUMBER OF YOUR CHOICE =>";K9
8081    OPEN FILE$ FOR APPEND AS #2
8082    PRINT #2, "CHANGE #";K9
8083    CLOSE #2
8084    CLS:COLOR 7,0
8085    IF K9 = 6 THEN RETURN
8090    ON K9 GOSUB 8300,8130,8150,8170,8180,8120,8200
8100    GOTO 8000
8120    RETURN
8130    INPUT "ENTER NUMBER OF COPPER SOLUTION ADDITIONS  =>";SPH
8140    RETURN
8150    INPUT "ENTER PRINT INTERVAL IN MINUTES =>";PI
8160    RETURN
8170    INPUT "ENTER NUMBER OF ELAPSED DAYS =>";DAY
8172    INPUT "ENTER INITIAL HOUR =>";IHR
8173    INPUT "ENTER INITIAL MINUTES =>";MIN
8174    INPUT "ENTER INITIAL SECONDS =>";ISEC
8175    RETURN
8180    INPUT "ENTER ALIQUOT SIZE FOR COPPER SOLUTION";M1
8190    RETURN
8200    COLOR 7,0:END
8300    M=200
8400    OUT DDRB,136
8430    PRINT "EMPTY(1)   FILL(2)"
8440    INPUT N
8441    IF N=1 THEN GOTO 8445
8442    IF N=2 THEN GOTO 8545
8443    RETURN
8445    FOR I=1 TO M
8450    OUT PB,1
8460    J=0
8470    OUT PB,0
8480    NEXT I
8490    GOTO 8430
8545    FOR I=1 TO M
8550    OUT PB,3
8560    J=0
8570    OUT PB,2
8580    NEXT I
8590    GOTO 8430
9100    IF HR > = IHR GOTO 9160
9110    IF F3 = 1 GOTO 9170
9120    DAY = DAY + 1
9140    F3 = 1
9150    GOTO 9170
9160    F3 = 0
9170    HR = HR + DAY*24 - IHR
9180    RETURN
10015   JJ = 0
10020   OPEN "LPT1:" AS #1
10025   PRINT #1,TS; TAB(25);AC; TAB(35); MV
10030   CLOSE #1
10035   END
```

```
'SAS PROGRAM CALCULATING 1-LIGAND CONCENTRATION FITTING FOR
 OCCU XAD-8 PH 6.2 COMPLEXOMETRIC TITRATIONS WITH PHTHALIC ACID'

filename joe '[mconklin.stat]';
filename file1 'sascorr.dat';

title 'cphth.dat 1 parameter fit of c1';

data joe.temp;
     infile file1;
     input cut 2-12 cu 13-21;
     cut=10**cut;
     cu=10**cu;
     keep cut cu;

proc nlin best=10 plot method=marquardt;
     parm    c1=-3.83;
     bounds c1<0;
     h=6.31e-7;
     k1=4.0;
     g1=10**c1*10**k1*cu/(1+cu*10**k1);
     model cut=cu+g1;
     der.c1=g1/10**c1;
     output out=b p=yhat r=yresid;
proc plot data=b;
     plot cut*cu='a' yhat*cu='p' /overlay vpos=25;
     plot yresid*cu / vref=0 vpos=25;
```

```
'SAS PROGRAM CALCULATING 2-LIGAND CONCENTRATIONS OF PHTHALIC ACID AND
 CATECHOL FOR OCGW XAD-8 PH 6.2 COMPLEXOMETRIC TITRATIONS'

libname joe '[mconklin.stat]';
filename file1 'sascorr.dat';

title 'cphthcat.dat 2 parameter fit: c1,c3';

data joe.temp;
     infile file1;
     input cut 2-12 cu 13-21;
     cut=10**cut;
     cu=10**cu;
     keep cut cu;
proc nlin best=10 plot method=marquardt;
     parm    c1=-4.25
             c3=-4.2;
     bounds c1<0,c3<0;
     h=6.31e-7;
     k1=4.0;
     k3=-7.96;

     g1=10**c1*10**k1*cu/(1+cu*10**k1);
     g3=10**c3*10**k3*cu/(h**2+cu*10**k3);
     model cut=cu+g1+g3;

     der.c1=g1/10**c1;
     der.c3=g3/10**c3;
     output out=b p=yhat r=yresid;
proc plot data=b;
     plot cut*cu='a' yhat*cu='p' /overlay vpos=25;
     plot yresid*cu / vref=0 vpos=25;
```

```
'SAS PROGRAM CALCULATING CONCENTRATIONS OF PHTHALIC ACID AND
 CATECHOL WITH A FIXED CONCENTRATION OF GLYCINE FOR BA XAD-8
 COMPLEXOMETRIC TITRATIONS AT PH 7.5'

libname joe '[mconklin.stat]';
filename file1 'ba7.dat';

title 'BA731ig.dat 2 parameter fit: c1,c3';

data joe.temp;
     infile file1;
     input cut 2-12 cu 13-21;
     cut=10**cut;
     cu=10**cu;
     keep cut cu;

proc nlin best=10 plot method=marquardt;
     parm     c1=-3.3
              c3=-5.3;
     bounds c1<0,c3<0;
     h=3.16228e-8;
     c4=-5.095;
     k1=4.0;
     k3=-7.96;
     k4=-1.24;

     g1=10**c1*10**k1*cu/(1+cu*10**k1);
     g3=10**c3*10**k3*cu/(h**2+cu*10**k3);
     g4=10**c4*10**k4*cu/(h+cu*10**k4);
     model cut=cu+g1+g3+g4;

     der.c1=g1/10**c1;
     der.c3=g3/10**c3;
     output out=b p=yhat r=yresid;
proc plot data=b;
     plot cut*cu='a' yhat*cu='p' /overlay vpos=25;
     plot yresid*cu / vref=0 vpos=25;
```

```
'SAS PROGRAM CALCULATING CONCENTRATIONS OF PHTHALIC ACID AND
 CATECHOL WITH A FIXED CONCENTRATION OF GLYCINE FOR BA XAD-8
 COMPLEXOMETRIC TITRATIONS AT PH 7.5'

libname joe '[mconklin.stat]';
filename file1 'ba7.dat';

title 'BA731iq.dat 2 parameter fit: c1,c3';

data joe.temp;
     infile file1;
     input cut 2-12 cu 13-21;
     cut=10**cut;
     cu=10**cu;
     keep cut cu;

proc nlin best=10 plot method=marquardt;
     parm    c1=-3.3
             c3=-5.3;
     bounds c1<0,c3<0;
     h=3.16228e-8;
     c4=-5.095;
     k1=4.0;
     k3=-7.96;
     k4=-1.24;

     g1=10**c1*10**k1*cu/(1+cu*10**k1);
     g3=10**c3*10**k3*cu/(h**2+cu*10**k3);
     g4=10**c4*10**k4*cu/(h+cu*10**k4);
     model cut=cu+g1+g3+g4;

     der.c1=g1/10**c1;
     der.c3=g3/10**c3;
     output out=b p=yhat r=yresid;
proc plot data=b;
     plot cut*cu='a' yhat*cu='p' /overlay vpos=25;
     plot yresid*cu / vref=0 vpos=25;
```

```
'SAS PROGRAM CALCULATING A THIRD LIGAND CONCENTRATION AND
 BINDING CONSTANT FOR OCGW XAD-8 PH 7.5 COMPLEXOMETRIC TITRATION'

libname joe '[mconklin.stat]';
filename file1 'ocgw7.dat';

title 'OC7flo.dat 2 parameter fit: c9,k9';

data joe.temp;
     infile file1;
     input cut 2-12 cu 13-21;
     cut=10**cut;
     cu=10**cu;
     keep cut cu;

proc nlin best=10 plot method=marquardt maxiter=30;
     parm    c9=-4.4 to -4.3 by 0.01
             k9=10;
     bounds c9<0,k9>5;
     h=3.16228e-8;
     c1=-4.3;
     c3=-4.85;
     k1=4.0;
     k3=-7.96;
     g1=10**c1*10**k1*cu/(1+cu*10**k1);
     g3=10**c3*10**k3*cu/(h**2+cu*10**k3);
     g9=10**c9*10**k9*cu/(1+cu*10**k9);
     model cut=cu+g1+g3+g9;

     der.c9=g9/10**c9;
     der.k9=g9/10**k9-(g9**k9/((10**k9)**2*10**c9));
     output out=b p=yhat r=yresid;
proc plot data=b;
     plot cut*cu='a' yhat*cu='p' /overlay vpos=25;
     plot yresid*cu / vref=0 vpos=25;
```

```
'SAS PROGRAM CALCULATING N-N-GLYCINE CONCENTRATION FOR
 BISCAYNE AQUIFER XAD-8 PH 6.2 COMPLEXOMETRIC TITRATION
 WITH CATECHOL AND PHTHALIC ACID '

libname joe '[mconklin.stat]';
filename file1 'ba6.dat';

title 'BA63ngly.dat 1 parameter fit: c8';

data joe.temp;
     infile file1;
     input cut 2-12 cu 13-21;
     cut=10**cut;
     cu=10**cu;
     keep cut cu;

proc nlin best=10 plot method=marquardt maxiter=10;
     parm    c8=-5.4 to -4.4 by .02;

     bounds c8<0;
     h=6.30957e-7;
     c1=-4.6395;
     c3=-5.2006;
     k1=4.0;
     k3=-7.96;
     k8=8.4;
     g1=10**c1*10**k1*cu/(1+cu*10**k1);
     g3=10**c3*10**k3*cu/(h**2+cu*10**k3);
     g8=10**c8*10**k8*cu/(1+cu*10**k8);
     model cut=cu+g1+g3+g8;

     der.c8=g8/10**c8;
     output out=b p=yhat r=yresid;
proc plot data=b;
     plot cut*cu='a' yhat*cu='p' /overlay vpos=25;
     plot yresid*cu / vref=0 vpos=25;
```

TYPICAL SAS PROGRAM OUTPUT

BA63ngly.dat 1 parameter fit:

NON-LINEAR LEAST SQUARES GRID SEARCH DEPEN

C8	RESIDUAL SS
-5.40	3.6742351307E-11
-5.38	3.7244576549E-11
-5.36	4.0456504235E-11
-5.34	4.6764982353E-11
-5.32	5.6600092189E-11
-5.30	7.0439597964E-11
-5.28	8.8813838906E-11
-5.26	1.1231110703E-10
-5.24	1.4158355818E-10
-5.22	1.7735370838E-10

BA63ngly.dat 1 parameter fit:

NON-LINEAR LEAST SQUARES ITERATIVE

DEPENDENT VARIABLE: CUT METHOD: MAR

ITERATION	C8	RSS
0	-5.4	3.67423
1	-5.4	3.67423

NOTE: CONVERGENCE CRITERION MET.

BA63ngly.dat 1 parameter fit: c8

NON-LINEAR LEAST SQUARES SUMMARY STATISTICS DEPENDENT VARIABLE CUT

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE
REGRESSION	1	3.015437E-09	3.015437E-09
RESIDUAL	35	3.674235E-11	1.049781E-12
UNCORRECTED TOTAL	36	3.052180E-09	
(CORRECTED TOTAL)	35	7.819497E-10	

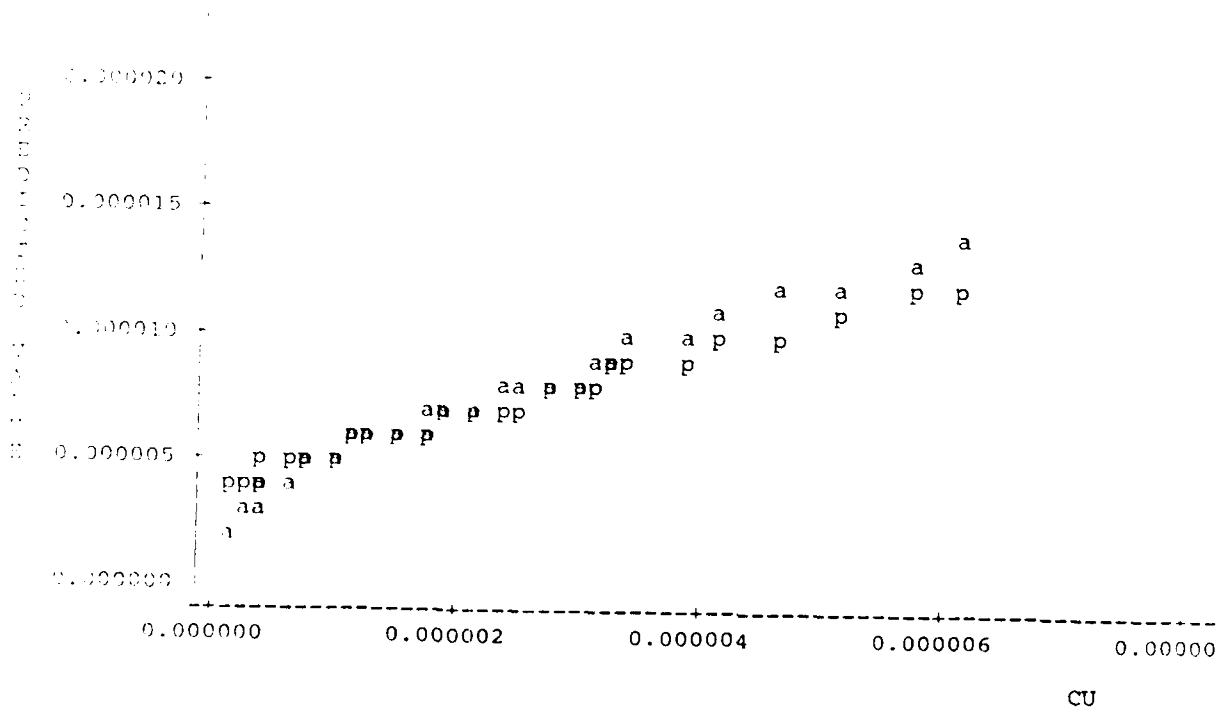
PARAMETER	ESTIMATE	ASYMPTOTIC STD. ERROR	ASYMPTOTIC 95 % CONFIDENCE INTERVAL LOWER	UPPER
C8	-5.399999944	1.717317E-07	-5.4000002928	-5.3999995952

ASYMPTOTIC CORRELATION MATRIX OF THE PARAMETERS

CORR	C8
C8	1.0000

BA63ngly.dat 1 parameter fit:

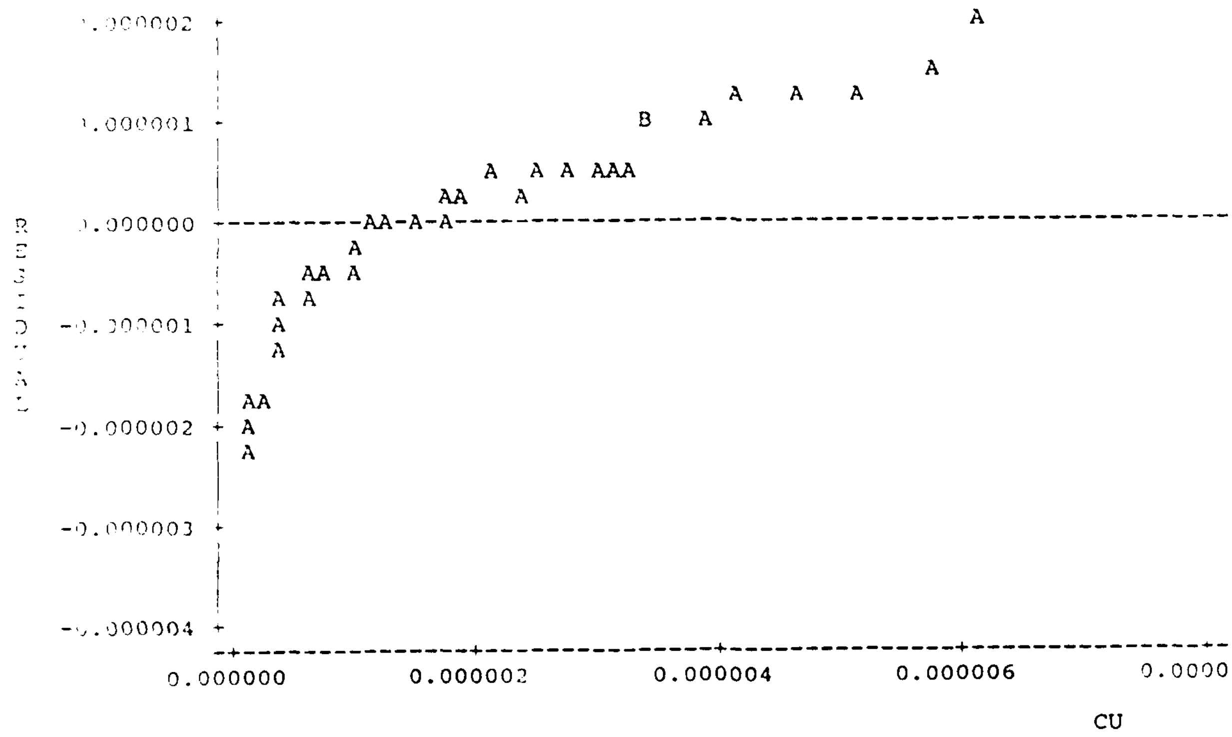
PLOT OF CUT*CU   SYMBOL USED
PLOT OF YHAT*CU   SYMBOL USED



NOTE: 13 OBS HIDDEN

BA63ngly.dat 1 parameter fit:

PLOT OF YRESID*CU   LEGEND: A = 1 OBS, B



TITRATOR DATA FILER - POTENTIOMETRIC TITRATION

OCGW 3Lig Poten 8:06 pm March 19, 1990

[gly]=1E-5M
[Phth]=5.5751E-5M [Cat]=1.415E-5M
Org-N=0.17 mg/L -OH=5 -COOH=19.7 meq/g C

Chemical Components: OCGW 3Lig Poten

#	Name	C1	Charge	Total	Initial	Log Free	Error
1	H2Phth	1	0	5.57510E-05	0.000	0.000	0.00000E+00
2	OH-	1	-1	-1.1050E-03	-11.000	0.000	0.00000E+00
3	Na+	1	1	1.00000E-02	0.000	0.000	0.00000E+00
4	NO3-	1	-1	1.00000E-02	0.000	0.000	0.00000E+00
5	H2Cat	1	0	1.41500E-05	0.000	0.000	0.00000E+00
6	HGly	1	0	1.00000E-05	0.000	0.000	0.00000E+00

Ionic Strength = 0.00000
Maximum iterations -- no convergence

Equilibrium Species: OCGW 3Lig Poten

#	Name	C1	H2Ph	OH-	Na+	NO3-	H2Ca	HGly	Log K	Molarity
1	H+	1	0	-1	0	0	0	0	-14.000	0.0000E+00
2	HPhth-	1	1	1	0	0	0	0	11.250	0.0000E+00
3	Phth--	1	1	2	0	0	0	0	20.320	0.0000E+00
4	HCat-	1	0	1	0	0	1	0	4.770	0.0000E+00
5	Cat--	1	0	2	0	0	1	0	5.770	0.0000E+00
6	H2Gly+	1	0	-1	0	0	0	1	-11.770	0.0000E+00
7	Gly-	1	0	1	0	0	0	1	4.420	0.0000E+00

OCGW 3-Lig 8:06 pm March 19, 1990

[Phth]=5.5751E-5M [Cat]=1.415E-5M
[Gly]=1E-5M @ Org-N=0.17mg/L
carboxylic=19.7meq/g C phenolic=5 meq/g C

Chemical Components: OCGW 3-Lig

#	Name	Cl	Charge	Total	Initial	Log Free	Error
1	Cu++	1	2	1.00000E-07	-12.000	0.000	0.00000E+00
2	NO3-	1	-1	1.00000E-02	0.000	0.000	0.00000E+00
3	Na+	1	1	1.00000E-02	0.000	0.000	0.00000E+00
4	Gly-	1	-1	1.00000E-05	0.000	0.000	0.00000E+00
5	Phth--	1	-2	5.57510E-05	0.000	0.000	0.00000E+00
6	Cat--	1	-2	1.41500E-05	0.000	0.000	0.00000E+00
7	H+	2	1	6.30960E-07	-6.200	0.000	0.00000E+00

Ionic Strength = 0.00000
Maximum iterations -- no convergence

Equilibrium Species: OCGW 3-Lig

#	Name	Cl	Cu++	NO3-	Na+	Gly-	Phth	Cat-	H+	Log K	Molarity
1	OH-	1	0	0	0	0	0	0	-1	-14.000	0.0000E+00
2	CuOH+	1	1	0	0	0	0	0	-1	-8.040	0.0000E+00
3	Cu(OH)2	1	1	0	0	0	0	0	-2	-16.330	0.0000E+00
4	Cu(OH)3-	1	1	0	0	0	0	0	-3	-26.300	0.0000E+00
5	Cu(OH)4-	1	1	0	0	0	0	0	-4	-39.400	0.0000E+00
6	(CuOH)2+	1	2	0	0	0	0	0	-2	-10.950	0.0000E+00
7	CuNO3+	1	1	1	0	0	0	0	0	0.500	0.0000E+00
8	Cu(NO3)2	1	1	2	0	0	0	0	0	-0.400	0.0000E+00
9	H2Gly+	1	0	0	0	1	0	0	2	11.3[illegible]	0.0000E+00
10	HGly	1	0	0	0	1	0	0	1	9.570	0.0000E+00
11	CuGly+	1	1	0	0	1	0	0	0	8.27[illegible]	0.0000E+00
12	CuGly2	1	1	0	0	2	0	0	0	15.13	[illegible]
13	HPhth-	1	0	0	0	[illegible]	1	0	1	4.3[illegible]	[illegible]
14	H2Phth	1	0	[illegible]	[illegible]	[illegible]	1	0	2	7.2[illegible]	[illegible]
15	CuPhth	1	1	0	[illegible]	[illegible]	1	[illegible]	0	4.[illegible]	[illegible]

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